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16. ABSTRACT

An analytical method was developed for the analysis of volatile priority pollutants in airstreams passing through wastewaters using a Tenax GC cartridge in combination with gas chromatography/mass spectrometry/computer. A sampling system was designed and field tested for sampling airstreams passing through grit chambers and activated sludge systems. Recovery of the volatile priority pollutants was accomplished by thermal desorption, purging with helium into a liquid-nitrogen-cooled nickel capillary trap, and releasing the vapors onto a gas chromatographic column. Characterization and quantification of the priority pollutants was accomplished by GC-mass spectrometry. The areas of investigation included: (a) the performance of a Tenax GC sampling cartridge for the priority pollutants in the airstreams passing through wastewaters; (b) the design, fabrication and evaluation of a field sampler; (c) recovery studies of priority pollutants from distilled water, raw wastewaters and activated sludge using laboratory-simulated conditions; (d) a methods-of-addition study for priority pollutants in raw wastewaters and activated sludge; (e) the delineation of the GC/MS/COMP operating parameters for priority pollutants collected on Tenax GC cartridges; (f) the application of the developed methods to the analysis of priority pollutants in airstreams passing through raw wastewaters and activated sludge, and (g) evaluation of the accuracy and precision of the collection methods.

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COLLECTION AND ANALYSIS OF PURGEABLE ORGANICS EMITTED FROM WASTEWATER TREATMENT PLANTS

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Contract No. 68-03-2681

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution of the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The study describes the development of an analytical method for the analysis of purgeable toxic organics which are airstripped from wastewater during treatment in wastewater treatment plants. The method is one of the tools needed to assess the fate and removability of priority organics entering wastewater treatment plants.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

An analytical method was developed for the analysis of volatile priority pollutants in airstreams passing through wastewaters using a Tenax GC cartridge in combination with gas chromatography/mass spectrometry/computer. A sampling system was designed and field tested for sampling airstreams passing through grit chambers and activated sludge systems. Recovery of the volatile priority pollutants was accomplished by thermal desorption, purging with helium into a liquid-nitrogen-cooled nickel capillary trap, and introducing the vapors onto a gas chromatographic column where they were separated from each other. Characterization and quantification of the priority pollutants was accomplished by mass spectrometry using mass fragmentography. The areas of investigation included: (a) the performance of a Tenax GC sampling cartridge for the priority pollutants occurring in the airstreams passing through wastewaters; (b) the design, fabrication and evaluation of a field sampler; (c) recovery studies of priority pollutants from distilled water, raw wastewater and activated sludge using laboratory-simulated conditions; (d) a methods-of-addition study for priority pollutants in raw wastewater and activated sludge; (e) the delineation of the GC/MS/COMP operating parameters for priority pollutants collected on Tenax GC cartridges; (f) the application of the developed methods to the analysis of priority pollutants occurring in airstreams passing through raw wastewater and activated sludge, and (g) evaluation of the accuracy and precision of the collection methods for "purgeable" priority pollutants in airstreams from raw wastewater and activated sludge basins.

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SECTION 1

INTRODUCTION

ROLE OF AERATION IN WASTEWATER TREATMENT

Aeration, the transfer of air into liquid, has many applications in the wastewater field. Aeration may occur naturally, for example at the air-liquid interface between wastewater and the air above it, or it may be induced, as by injection of air into the wastewater or by mechanical agitation of the wastewater to increase its exposure to the atmosphere. In induced aeration, the gas phase may be provided directly from the atmosphere (mechanical aeration), by compressed air (diffusion or injection aeration), or by compressed oxygen (pure oxygen process).

Aeration is commonly used in biological wastewater treatment to provide the oxygen needed by activated sludge organisms for aerobic decomposition and to induce turbulence so that the sludge remains in suspension, in intimate contact with food and oxygen. Forced aeration may also be used solely for agitation. These applications will be described in greater detail below.

Another application of aeration is in removing gases and other volatile substances from water or wastewater. This application is generally utilized for water treatment processes, such as removal of CO_2 before lime-soda softening, removal of H_2S, and removal of odor and taste producing substances secreted by microorganisms. A major application in the wastewater field is air stripping of ammonia from domestic or industrial wastewaters.

The aeration systems examined during the course of this project were designed to provide agitation alone (aerated grit chamber) or to provide both oxygen and agitation (activated sludge). Removal of gases and volatiles was not an objective. However, since the physical and chemical conditions were appropriate for such gas transfer, it might be expected to occur.

TYPES OF REACTORS EMPLOYED IN WASTEWATER TREATMENT

The principal reactor types used in wastewater treatment are (1) plug flow reactor, (2) complete-mix reactor, and (3) arbitrary flow reactor (1). In plug flow, aliquots of wastewater enter the tank, pass through it, and are discharged in the same sequence in which they enter. Each aliquot retains its identity and each remains in the tank for the same length of time. In a treatment system utilizing plug flow, one would expect the concentration of wastewater components to be highest at the influent (input) end and lowest at the effluent (exit) end. Plug flow reactors are generally long tanks with a high length:width ratio. In complete mix reactors, incoming aliquots are almost immediately dispersed throughout the tank. The concentration of wastewater components would be approximately the same at any point within the reactor. To facilitate complete mixing, the reactors are generally round or square.

In practice, ideal plug-flow or complete mix rarely occurs. Despite design of the reactors, some degree of partial mixing occurs, resulting in something intermediate between the two. This is designated "arbitrary flow."

AIR INTRODUCTION DEVICES

A wide variety of aeration devices is available (1-3). The two major categories applicable to induced (forced) aeration of wastewaters are (1) subsurface diffusers and (2) mechanical aerators.

In the first category, compressed air (or oxygen) is introduced into the tank by means of coarse-bubble (nozzles, spargers) or fine-bubble (porous plates and tubes) devices. While fine bubbles are theoretically more efficient for gas transfer, in practice they tend to clog easily and to enhance foaming. Compressed air may be introduced at or near the bottom, or at one side to encourage spiral movement.

In mechanical aerators, the objective is to put the wastewater into greater contact with the atmosphere. This can be accomplished by surface paddles, submerged paddles, partially submerged rotating brushes, propeller blades so located as to aspirate air down into the water, turbine blades which draw the wastewater up and spray it over the surface, or other devices (4).

APPLICATIONS OF AERATION

Aeration may be employed in wastewater treatment for agitation and/or oxygen transfer, depending on the objective of the unit process.

Aerated Grit Chamber

Wastewater often contains sand, cinders, gravel, fruit pits, and other inert heavy particles which might damage pumps and other mechanical equipment, create deposits in pipes and channels, and accumulate in the digester. Therefore, grit removal is generally one of the first processes applied to wastewater, being preceded only by coarse (bar) screening and/or comminution. Ideally, grit chambers should remove only heavy inorganic materials, leaving the organics to be degraded in subsequent treatment. In the conventional grit chamber, still in use at most wastewater treatment plants, the grit chamber relies on gravity and slightly reduced flow rate ($\sim$1 fps or 0.3 m/s) to remove particles with a specific gravity of 2.65 and diameter of 2×10^{-2} cm (3,4). Because some organic material is also deposited, the collected grit may have to be washed before disposal. Since grit removal is performed at the point at which the wastewater is at its maximum strength, septic conditions accompanied by odor production are common in grit chambers.

The aerated grit chamber was designed to accomplish a higher degree of grit removal, to reduce odors, and to wash the organic material from the grit. The most effective aerated grit chambers induce a spiral flow by injecting air 18-24 inches above the bottom along one side of the chamber (1). Detention time of the wastewater is ∿3 min. Since aeration occurs at the point of maximum wastewater strength, substantial transfer of gases and volatiles might be expected to occur. In practice these systems require careful adjustment of air velocity to ensure removal of the grit without sedimentation of the lighter organic particles. A representative air velocity is 5 cfm of air per foot of tank length (1).

Biological Processes

Primary treatment of municipal domestic wastewater is generally accomplished by physical processes such as gravity sedimentation and flotation. Dissolved and finely divided materials are not removed in these processes. Biological (secondary) wastewater treatment is designed to remove pollutants from wastewater by sorption to biological films (as in trickling filters) or to biological floc (as in activated sludge).

In the activated sludge process, nonsettleable substances are converted into biological floc (sludge) which can be removed by sedimentation, or into stable, mineralized endproducts which have a lower oxygen demand. This process is most commonly conducted in complete mix reactors with forced aeration systems, although many variations exist. The process is dependent on bringing a large concentration of active organisms (mixed liquor suspended solids of about 2500 mg/ℓ) into intimate contact with food (organics) and oxygen. Aeration provides the desired turbulence and oxygenation.

To provide the sludge with adequate oxygen, it is generally agreed that at least 0.5 mg/ℓ of dissolved oxygen (DO) should be present at all times in all parts of the aeration tank.

In conventional activated sludge plants, aeration is accomplished with air. For municipal wastewater, air requirements are about 0.8 - 1.5 ft^3 per gal of wastewater. However, aeration requirements vary according to strength of the wastewater, and estimation of air requirements is based preferably on the biochemical oxygen demand (BOD), being about 1000 ft^3 of air per pound of BOD in the influent wastewater. Regardless of strength, a minimum air flow of ∿3 cfm/ft of tank length must be provided to prevent settling.

Conventional activated sludge systems, especially those located in warm or temperate climates, are generally open to the atmosphere.

The maximum dissolved oxygen concentration which can be obtained with air aeration is limited by the partial pressure of the oxygen in the air. Higher DO concentrations can be obtained if pure oxygen is used in aeration. After development of cost-effective on-site oxygen production processes, the pure oxygen activated sludge process came into use in the early 1970's. In this system high purity oxygen is injected into aeration tanks and is quickly dispersed with mixers, allowing rapid and efficient gas transfer. Since higher concentrations of activated sludge can be maintained, the required detention time can be reduced. Because of this, the oxygen process is frequently adopted to upgrade and increase the capacity of existing activated sludge plants. To assure most cost-effective use of the oxygen, pure oxygen activated sludge tanks are covered and the oxygen is recirculated. The complete mix reactor is generally used, but the process can also be applied to overloaded plug-flow systems (1).

DESCRIPTION OF LOCAL MUNICIPAL TREATMENT FACILITIES

Testing was conducted at municipal wastewater treatment plants in North Carolina and Virginia. Plants were selected on the basis of (1) type of aeration and (2) proximity to Research Triangle Institute.

Mason Farm Wastewater Treatment Plant, Chapel Hill, NC

The Mason Farm Wastewater Treatment plant treats wastewater from the towns of Chapel Hill and Carrboro. There is essentially no industry in the area, and extensive records kept by the Town of Chapel Hill and the UNC Wastewater Research Center characterize the wastewater as a "typical domestic sewage." A flow diagram of the plant is shown in Figure 1. Typical flow is 4.8-5 mgd. The plant is noteworthy because of the dual, identical treatment trains in the older part of the plant. Units include:

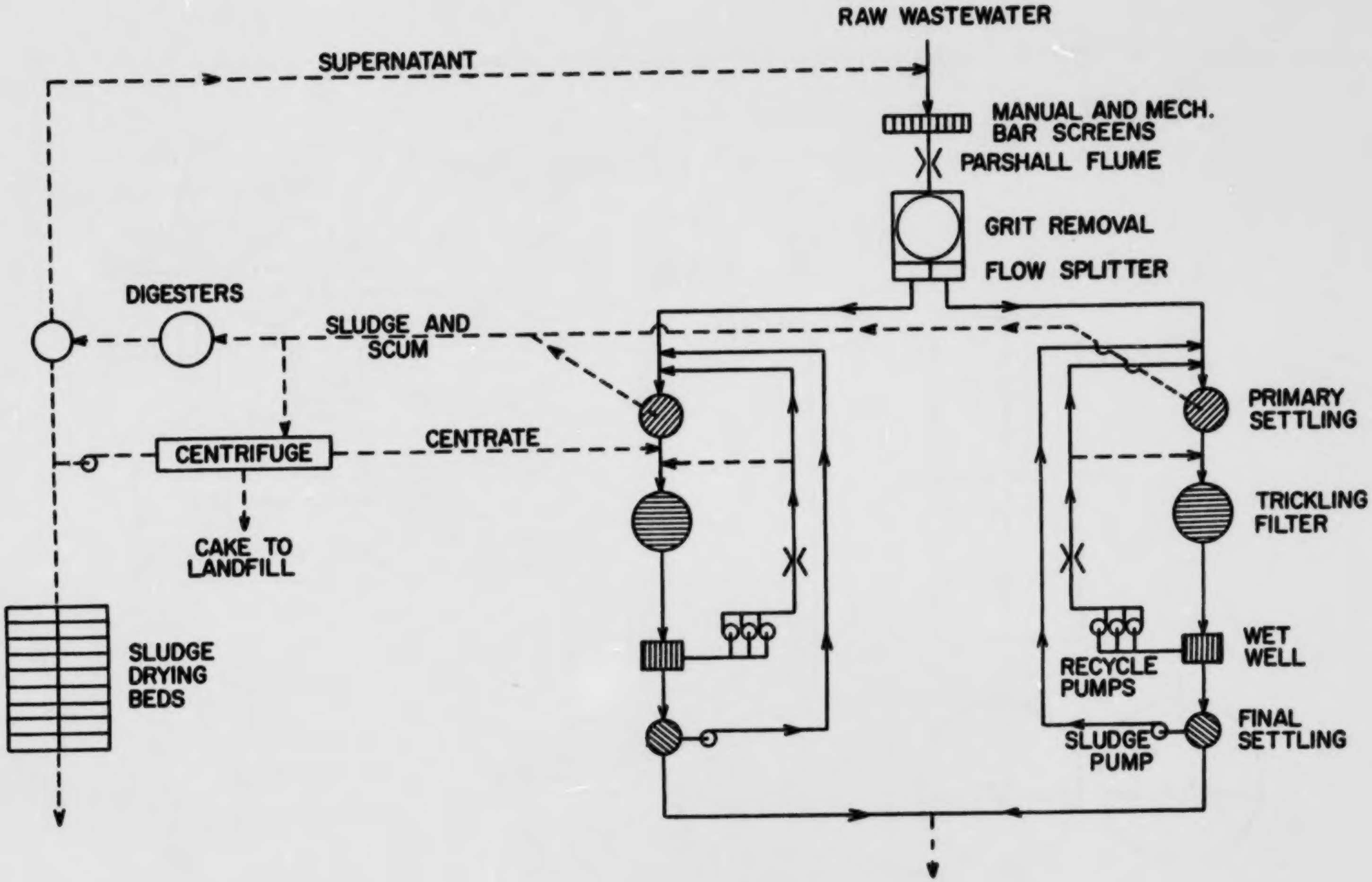
(1) Mechanical bar screen
(2) Conventional grit chamber
(3) Primary settling basins
(4) Alum injection for phosphate removal
(5) High rate trickling filters
(6) Intermediate settling basins
(7) Activated-sludge type nitrification system
(8) Final settling basins
(9) Chlorination chamber
(10) Two-stage anaerobic digestors.

Samples for this project were taken over the conventional grit chamber.

Northside Treatment Plant, Durham, NC

The Northside Treatment Plant treats wastewater from homes, businesses, and industries in the northeast side of Durham. Typical flow is 6.3 mgd. A diagram of the plant is shown in Figure 2. Units include:

(1) Coarse screening (mechanical bar screen)
(2) Grit removal and flotation of grease in a vacuum process (Vacuator)
(3) Roughing trickling filtration
(4) Primary sedimentation
(5) Conventional activated sludge with 6-8 hr detention and forced air diffusion (observation of the tanks indicates that the flow pattern is arbitrary, somewhere between plug flow and complete mix)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MANUAL AND MECH.
BAR SCREENS
PARSHALL FLUME
GRIT REMOVAL
FLOW SPLITTER
DIGESTERS
SLUDGE AND
SCUM
CENTRIFUGE
CENTRATE
CAKE TO
LANDFILL
PRIMARY
SETTLING
TRICKLING
FILTER
WET
WELL
RECYCLE
PUMPS
FINAL
SETTLING
SLUDGE
PUMP
SLUDGE
DRYING
BEDS

Figure 1. Mason Farm Wastewater Treatment Plant.

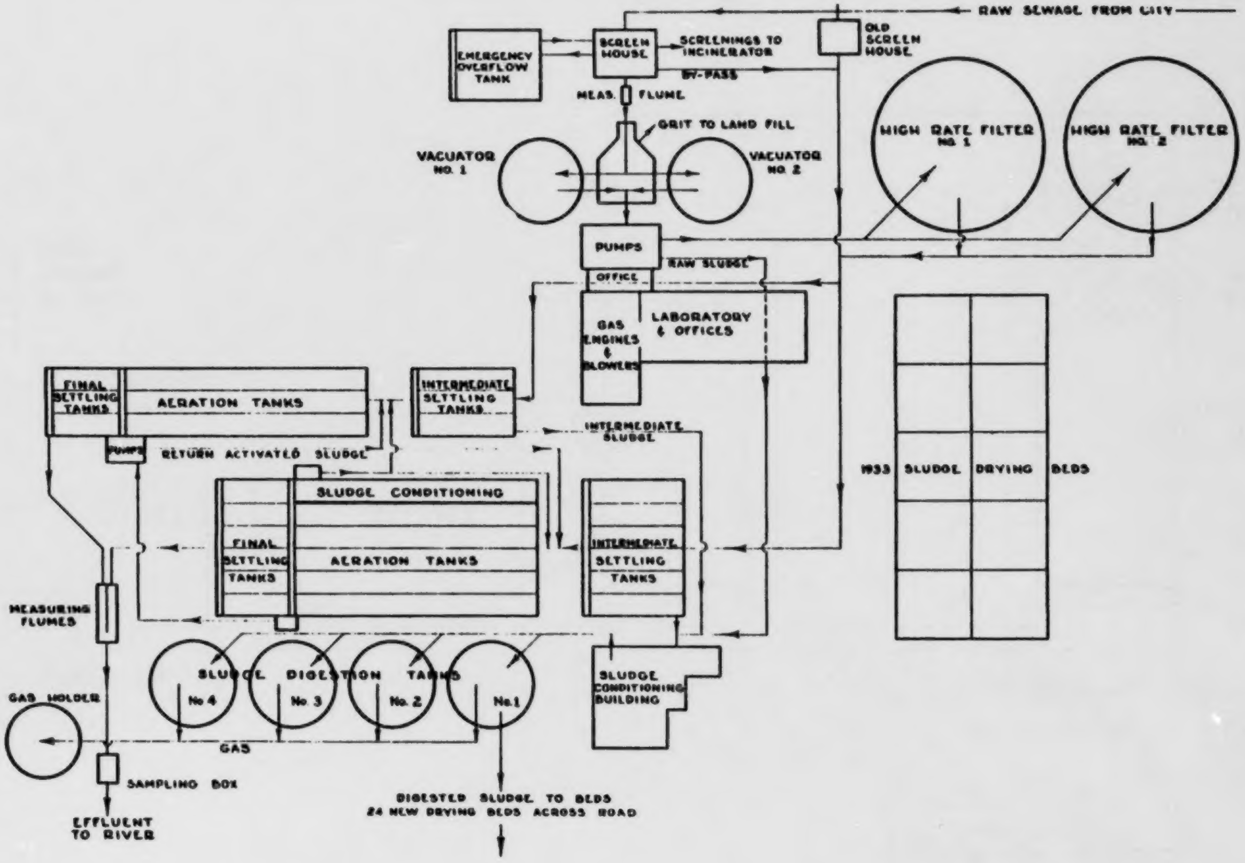

RAW SEWAGE FROM CITY
OLD SCREEN HOUSE
EMERGENCY OVERFLOW TANK
SCREEN HOUSE
SCREENINGS TO INCINERATOR
BY-PASS
MEAS. FLUME
GRIT TO LAND FILL
VACUATOR NO. 1
VACUATOR NO. 2
HIGH RATE FILTER NO. 1
HIGH RATE FILTER NO. 2
PUMPS
RAW SLUDGE
OFFICE
GAS ENGINES & BLOWERS
LABORATORY & OFFICES
FINAL SETTLING TANKS
AERATION TANKS
INTERMEDIATE SETTLING TANKS
INTERMEDIATE SLUDGE
PUMPS
RETURN ACTIVATED SLUDGE
1933 SLUDGE DRYING BEDS
SLUDGE CONDITIONING
FINAL SETTLING TANKS
AERATION TANKS
INTERMEDIATE SETTLING TANKS
MEASURING FLUMES
SLUDGE DIGESTION TANKS
No 4
No 3
No 2
No 1
SLUDGE CONDITIONING BUILDING
GAS HOLDER
GAS
SAMPLING BOX
EFFLUENT TO RIVER
DIGESTED SLUDGE TO BEDS
24 NEW DRYING BEDS ACROSS ROAD

Figure 2. Flow diagram of Northside Sewage Treatment Plant, Durham, NC.

(6) Secondary sedimentation with sludge recycle
(7) Chlorination
(8) Anaerobic sludge digestion

This plant was used for preliminary experiments required for design of the sampling system. Samples were taken at the influent end of the aeration tanks. These tanks are each 15 x 200 ft with a depth of 13 ft. Liquid depth is ∿11.5 ft. Air is injected into each tank by 344 porous plates, 12 x 12 in., set vertically in double rows in a header placed 12 in. above tank bottom.

Northside Facility, City of Danville, VA

The Northside Plant treats domestic and industrial wastewater from the City of Danville. Unit processes include:

(1) Screening
(2) Grit removal
(3) Preaeration and grease floatation
(4) Primary sedimentation
(5) Pure oxygen activated sludge
(6) Secondary sedimentation
(7) Disinfection

A diagram of the plant is shown in Figure 3. The facility, completed in 1976, serves a population of ∿50,000 and treats municipal and industrial wastewater. The plant has a nominal flow capacity of 24 mgd and is currently treating ∿18 mgd. Approximately 60% of the flow comes from industries, including textile manufacturing, rubber manufacturing, glass manufacturing, and tobacco products. The plant utilizes the Unox process (Union Carbide). Oxygen is produced on-site by the pressurized swing adsorption (PSA) process. The pure oxygen aeration chamber is completely enclosed and is operated under pressure. The pressurized oxygen feeds into the chamber above the liquid surface. Agitation and oxygenation are accomplished by mixers located just below the surface and just above the bottom. The system is vented through a stack above the aeration chamber. For this project, a sample was taken of the vent gas.

South Burlington Plant, Burlington, NC

The South Burlington Plant treats municipal and industrial wastewater from the southern half of Burlington, NC. The average flow is ∿5.5-6.0 mgd, ∿35-40% of which is industrial. The population equivalent is ∿28,000. The major organic load comes from the textile industries in the area. This plant has an aerated grit chamber, but the aeration is used only infrequently due to operational difficulties in adjusting the air flow. Air is provided by coarse tube-type diffusers. Secondary treatment is provided by conventional activated sludge with a nominal 8 hr detention period. Air in the influent end of the 4 tanks is provided through plastic nozzles located about 1 ft above the bottom of the tank. At the other end of each tank, mechanical aerators of the updraft type provide aeration and agitation.

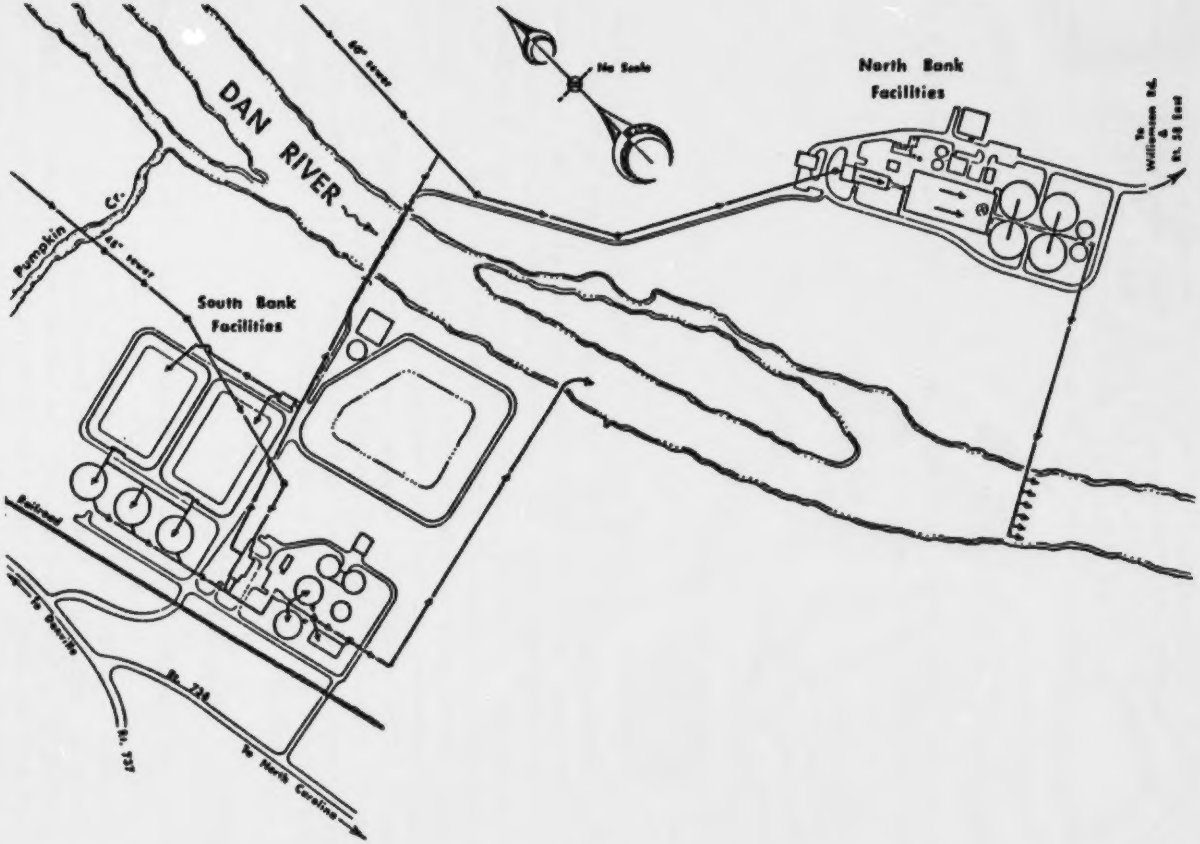

No Scale
North Bank
Facilities
To
Williamson Rd.
&
Rt. 58 East
60" sewer
DAN RIVER
Pumpkin Cr.
48" sewer
South Bank
Facilities
Railroad
To Danville
Rt. 726
Rt. 737
To North Carolina

Figure 3. Water pollution control facilities, City of Danville, VA.

At this plant, samples were taken above the aerated grit chamber (while the aeration system was in operation) and above the influent end of the AS aeration tanks.

SECTION 2

CONCLUSIONS

Volatile priority pollutants were concentrated from air streams passing through wastewaters on Tenax GC sorbent in a short glass tube. Recovery of the volatile priority pollutants was accomplished by thermal desorption, purging with He into a liquid-nitrogen cooled nickel capillary trap, and introducing the vapors into a gas chromatographic column where the vapors are separated from each other. Characterization and quantification of the priority pollutants were accomplished by mass spectrometry using mass fragmentography.

The linear dynamic range for analysis of priority pollutants depended upon two principal phenomena. The first was a function of breakthrough volume for each pollutant trapped on the Tenax GC sampling cartridge and the second was related to the inherent sensitivity of the mass spectrometer for each organic compound. Thus the range and sensitivity varied considerably from one priority pollutant to another. The linear range for the quantitation on a gas chromatograph/mass spectrometer/computer (GC/MS/COMP) was generally three orders of magnitude and was principally dependent upon the linearity of the A/D converter (interface) of the GC/MS computer system.

At the present time there are no known potential interferences to quantification using the developed collection and analysis system. The use of a specified, packed, glass chromatographic column in combination with selective ion chromatography provide sufficient specificity for the analysis of volatile priority pollutants.

The accuracy and reproducibility of this method was ±10% to ±30% as determined by the relative standard deviation for the different substances when replicate sampling cartridges were examined. The inherent analytical error was a function of several factors: (1) ability to accurately determine the breakthrough volume for each of the identified organics; (2) the accurate measurement of the volume of the air stream sampled; (3) the percent recovery of the organic priority pollutant from the sampling cartridge after storing; (4) the reproducibility of thermally desorbing compounds from the Tenax cartridge and their introduction into the analytical system; (5) the accuracy achieved in determining the relative molar response ratios between the identified substance (priority pollutant) and the external standards (perfluorobenzene and perfluorotoluene) used for calibrating the analytical system; (6) the reproducibility achieved in transmitting the sample through a gas chromatographic column and (7) the day-to-day reliability of the MS/COMP system.

The accuracy of the analysis for Tenax cartridges containing priority pollutant was generally ±30%.

GC/MS analysis was extremely sensitive and specific for volatile priority pollutants in air streams from wastewaters of municipal wastewater treatment plants. The sensitivity was generally between 1-10 ng/ℓ of air. The combination of the gas chromatographic column and the selection of specific or unique ions (representing the various compounds of interest identified in the samples) yielded a relatively specific assay for these priority pollutants.

Because some of the compounds of interest may be hazardous to man, it is extremely important to exercise safety precautions in the preparation and disposal of liquid and gas standards, cleaning of used glassware, etc.

SECTION 3

RECOMMENDATIONS

Several major research tasks should be expanded and pursued: (1) further research should be conducted on the storage of field samples containing priority pollutants on Tenax GC cartridges in order to precisely define the expected recoveries; (2) The accuracy of sampling should be determined by spiking the air streams from the wastewaters with known amounts of priority pollutants to determine whether the substances are accurately collected; (3) Since the capacity of a Tenax GC sampling cartridge might be exceeded by the total pollutant load in the sample, displacement chromatography experiments need to be performed; (4) The efficiency in transferring pollutants emitted from air streams to the sampling manifold via the umbilical cord should be further evaluated and (5) The design of the sampling head should be perfected for convenient use at aeration ponds and grit chambers.

SECTION 4

PROGRAM OBJECTIVES

The objectives of this research program were to develop procedures to representatively sample air streams passing through wastewaters in grit chambers and aeration basins at municipal wastewater treatment facilities and to analyze representative samples for volatile toxic organic pollutants.

The specific aim was to evaluate three types of aeration systems in order to develop the required sampling procedures. The types of aeration systems examined were: (1) pure oxygen [closed chamber]; (2) totally mixed activated sludge basin and (3) plug-flow basins. The method employed a trap and inject approach for quantification using gas chromatography/mass spectrometry/computer.

The purpose of the program was also to establish the accuracy, precision and sensitivity of the analytical procedures developed by adding known quantities of at least 25 of the toxic organics (priority pollutants) to wastewater in laboratory or pilot vessels simulating the aeration processes in wastewater plants. Using the developed and evaluated procedures, the final aim was to apply the methodology to the analysis for priority pollutants in air streams passing through wastewater at several municipal plants.

SECTION 5

EVALUATION OF TENAX GC SAMPLING CARTRIDGES FOR USE WITH PRIORITY POLLUTANTS

INTRODUCTION

In order to quantitatively collect volatile priority pollutants from air streams passing through wastewaters onto a solid sorbent such as Tenax GC, several facets of the technique need to be evaluated. The collection of priority pollutants on a sampling cartridge, followed by thermal desorption and GC with mass spectrometric detection, permits the sensitive detection and quantification of adsorbable vapors.

When polluted gas enters a sorbent bed such as occurs during air sampling, an equilibrium zone is established near the point of entry which, as more pollutant vapor is introduced, may expand through the packing length until the capacity of the sorbent is exceeded. Also, if after an initial period of time, additional polluted vapors are introduced, then as the purging of the packing bed continues, the zones of vapors will move through the packing bed. When the zones reach the end of the available packing bed and the vapors begin to leave, breakthrough has occurred. Thus breakthrough volume is simply the elution volume (V_e) which can be calculated if the time required for the zone to migrate and elute from the sorbent bed and the sampling rate are known. In an ideal collection system, breakthrough volume has an infinite value at ambient temperature. The relationship which describes the amount of vapor adsorbed to a given quantity of adsorbent as a function of pressure, temperature and concentration of the solute vapor is given by the Langmuir equation which has been previously discussed (5,6). The breakthrough volumes for a series of representative volatile (purgeable) priority pollutants were determined.

Since the humidity of the air streams passing through wastewaters will reach essentially 100%, the trapping of residual amounts of water vapor on Tenax GC will occur. Thus, the effect of the residual water on recovering priority pollutants needed evaluation. Also, water vapor might affect the efficient transfer of organic vapors from the sampling device to the analytical column.

Finally, recovery of priority pollutants from the sorbent as a function of storage time needed study since immediate analysis is not always possible.

This section examines the potential problems associated with (1) breakthrough volume, (2) recovery of priority pollutants from the collection device as a function of storage time, and (3) the effect of drying sampling cartridges with calcium sulfate prior to their analysis.

EXPERIMENTAL

Determination of Breakthrough Volumes

Breakthrough volumes were estimated for a number of "purgeable" priority pollutants. Determining the elution volume for the priority pollutant on a gas chromatographic column packed with the sorbent, Tenax GC, was the method of choice (6,7,8). A 3 mm-i.d. x 3.05-m stainless steel column was used. After injecting each vapor mixture, the elution volume was determined for each of the individual compounds as the product of flow rate and elution time. A series of injections was made at decreasing temperatures, and a plot of the log $1/v_e$ vs. temperature was constructed. Using linear regression analysis, the breakthrough volumes (50% loss) at several ambient temperatures were determined by extrapolation. The standard cartridge dimensions employed in the field are 1.5-cm i.d. x 6.0-cm bed length.

This technique for determining breakthrough volumes has been compared with other techniques and is considered a viable rapid approach for the determination of breakthrough volumes (5-8).

Preparation of Tenax GC Sampling Cartridges

All glassware, sampling tubes (Pyrex glass, 1.5 cm i.d. x 10 cm in length), cartridge holders (Kimax®), etc., were washed in Isoclean/water, rinsed with deionized-distilled water then acetone, and air-dried. Glassware was heated to 450-500°C for 2 hr to insure that all organic material was removed prior to its use.

Virgin Tenax GC was extracted in a Soxhlet apparatus for a minimum of 18 hrs, each, with pentane and methanol (10). The Tenax GC sorbent (Applied Science, State College, PA) was dried in a dry-box with nitrogen purging to remove excess solvent and then was dried further in a vacuum oven at 100°C for 3-5 hrs. All operations hereafter must be carried out in a room free of organic vapors from laboratories, etc. Tenax GC was sieved to provide a fraction corresponding to 35/60 mesh. This fraction was used for preparing sampling cartridges throughout the study. In those cases where sampling cartridges of Tenax GC were recycled, the adsorbent was again extracted in a Soxhlet apparatus with methanol as described for the virgin material, as well as with a non-polar solvent, n-pentane, in order to remove the relatively non-polar and non-volatile materials which may have accumulated on the sorbent bed during previous uses.

Tenax GC cartridge samplers were then prepared (10-cm long x 1.5-cm i.d. glass tubes containing 6.0-cm sorbent anchlored with glass wool plugs) and conditioned at 270°C with helium flow at 30 ml/min for 1 hr. The conditioned cartridges were transferred to Kimax® (2.5 cm x 157 cm) culture tubes; immediately sealed using Teflon® inserts in aluminum lined caps, and cooled (8-10). The Kimax® containers were placed in a metal-sealable can (e.g., paint can) to minimize contamination. Cartridges prepared in this manner retained a low "background" of organics for a period of six weeks.

Gas-Liquid Chromatography

Gas-liquid chromatography (GC) was conducted on a Varian 3700 series gas chromatograph (Varian Instr. Inc., Walnut Creek, CA) equipped with dual flame ionization detectors. A previously described thermal desorption unit (Figs. 4,5) was used for transferring adsorbed vapors from the Tenax GC sampling cartridges to the analytical column (11,12). The analytical column was a 100-m, glass support-coated open-tubular (SCOT) capillary coated with OV-101 stationary phase. The SCOT column was programmed from 30°C to 240°C at 4°/min. Carrier gas (helium), hydrogen and air flows were 3, 30, and 200 ml/min, respectively. The detector temperature was maintained at 250°C.

Table 1 presents the operating parameters for the thermal desorption unit and the GC.

Calibration Techniques

For the purpose of calibrating instruments for quantitative evaluation studies of priority pollutants throughout this program, it was necessary to accurately spike Tenax GC sampling cartridges with known amounts of priority pollutants and the internal standards, perfluorobenzene and perfluorotoluene. Figure 6 depicts the permeation system which was used for accurately delivering known concentrations of air/vapor mixtures to the Tenax GC cartridges. The performance of this permeation system has previously been described (9,13).

Table 2 provides a list of the priority pollutants, the materials used for constructing permeation tubes and the permeation rates which were established by gravimetric means (9,13).

Data Analysis

The gas-liquid chromatograph was calibrated by analyzing a series of Tenax GC cartridges which were loaded with known amounts of priority pollutants from the permeation system. For the purpose of determining the percent recoveries and subsequent studies, the response of the gas chromatograph to each of the priority pollutants was used in order to determine the quantity of the priority pollutant for each experimental condition. Either peak height or area was used for quantification. Varian CDS-11 and Spectra-Physics integrators were used for determining peak areas.

Storage Studies

Tenax GC sampling cartridges (1.5-cm i.d. x 6.0-cm bed length) were loaded with calibrated amounts (400-800 ng/cartridge) of priority pollutants

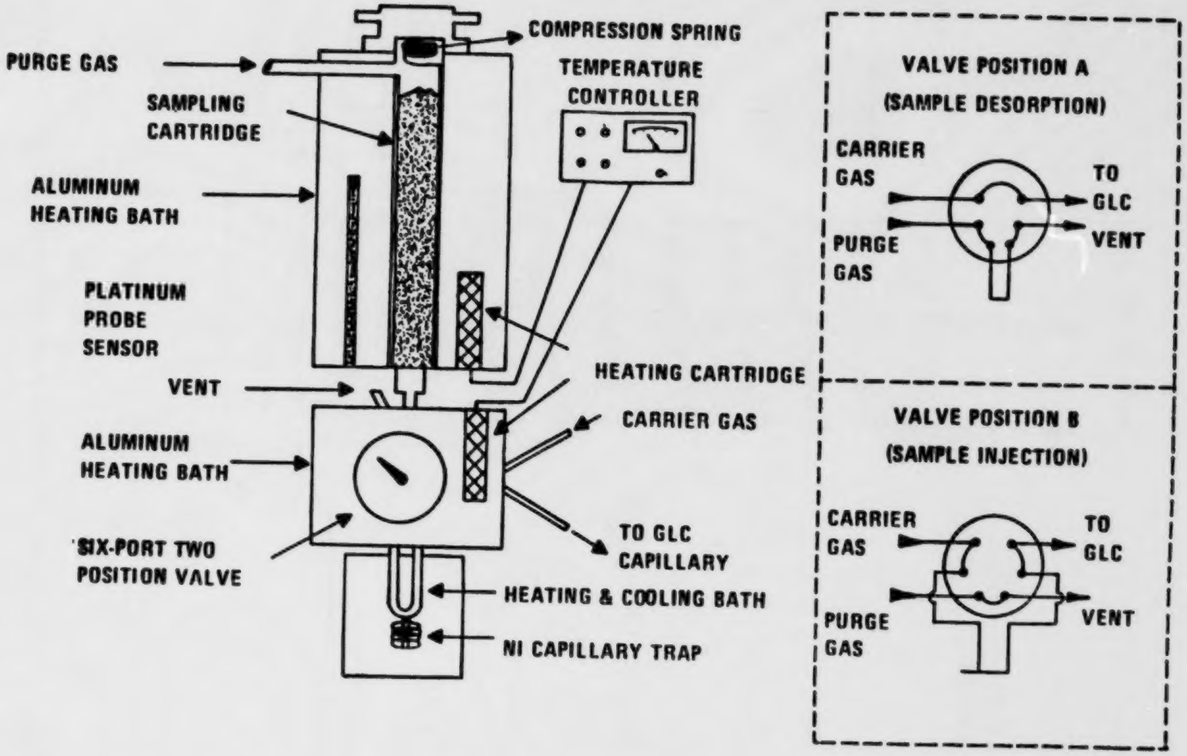

PURGE GAS
SAMPLING CARTRIDGE
ALUMINUM HEATING BATH
PLATINUM PROBE SENSOR
VENT
ALUMINUM HEATING BATH
SIX-PORT TWO POSITION VALVE
COMPRESSION SPRING
TEMPERATURE CONTROLLER
HEATING CARTRIDGE
CARRIER GAS
TO GLC CAPILLARY
HEATING & COOLING BATH
NI CAPILLARY TRAP
VALVE POSITION A
(SAMPLE DESORPTION)
CARRIER GAS
PURGE GAS
TO GLC
VENT
VALVE POSITION B
(SAMPLE INJECTION)
CARRIER GAS
PURGE GAS
TO GLC
VENT

Figure 4. Thermal desorption inlet-manifold.

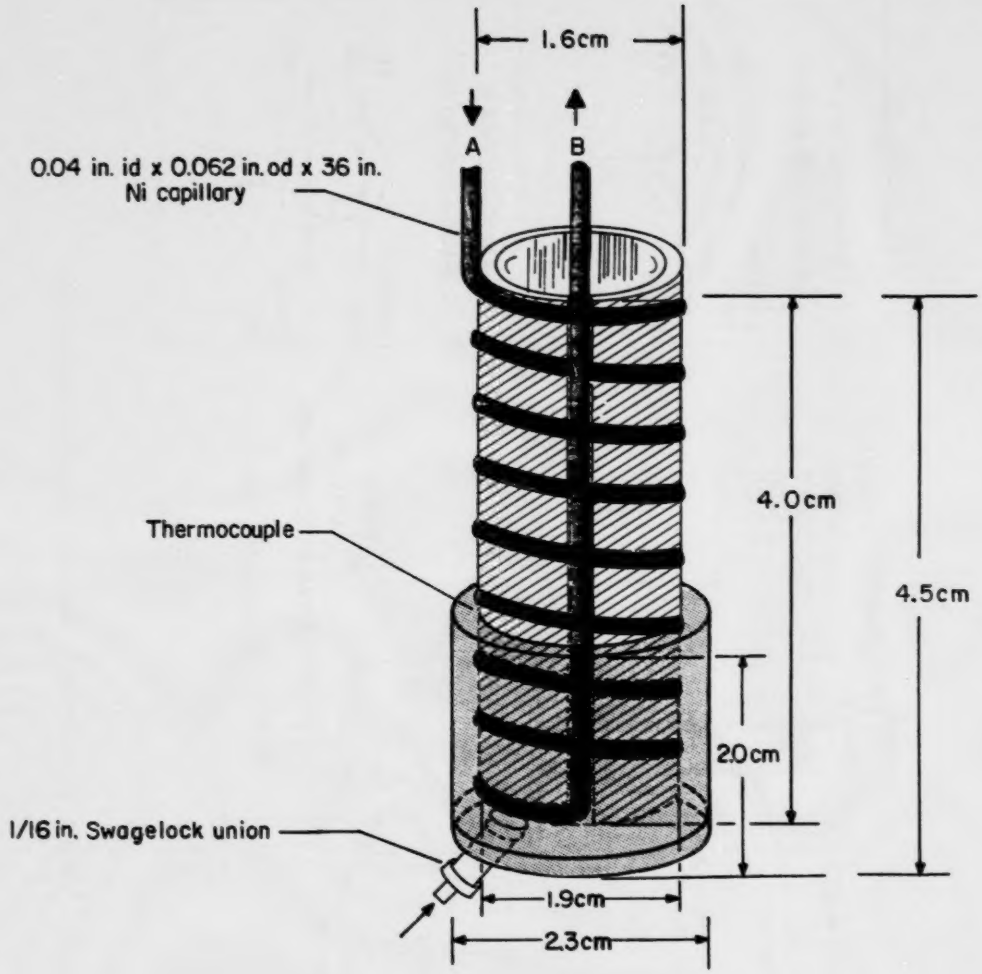

1.6cm
A
B
0.04 in. id x 0.062 in. od x 36 in.
Ni capillary
Thermocouple
4.0cm
4.5cm
2.0cm
1/16 in. Swagelock union
1.9cm
2.3cm

Figure 5. Cryo-heater module for inlet-manifold (12).

TABLE 1. PARAMETERS FOR INLET-MANIFOLD AND GAS-LIQUID CHROMATOGRAPHY

Parameter	Condition
Inlet-manifold	
desorption chamber and valve	270°C
capillary trap - trap cycle	-195°C
inject cycle	+250°C
thermal desorption time	8 min
He purge rate	15 ml/min
GLC	
column (100-m OV-101 SCOT)	30-240°C at 4°C/min
He carrier flow	3.0 ml/min
FID temperature	250°C

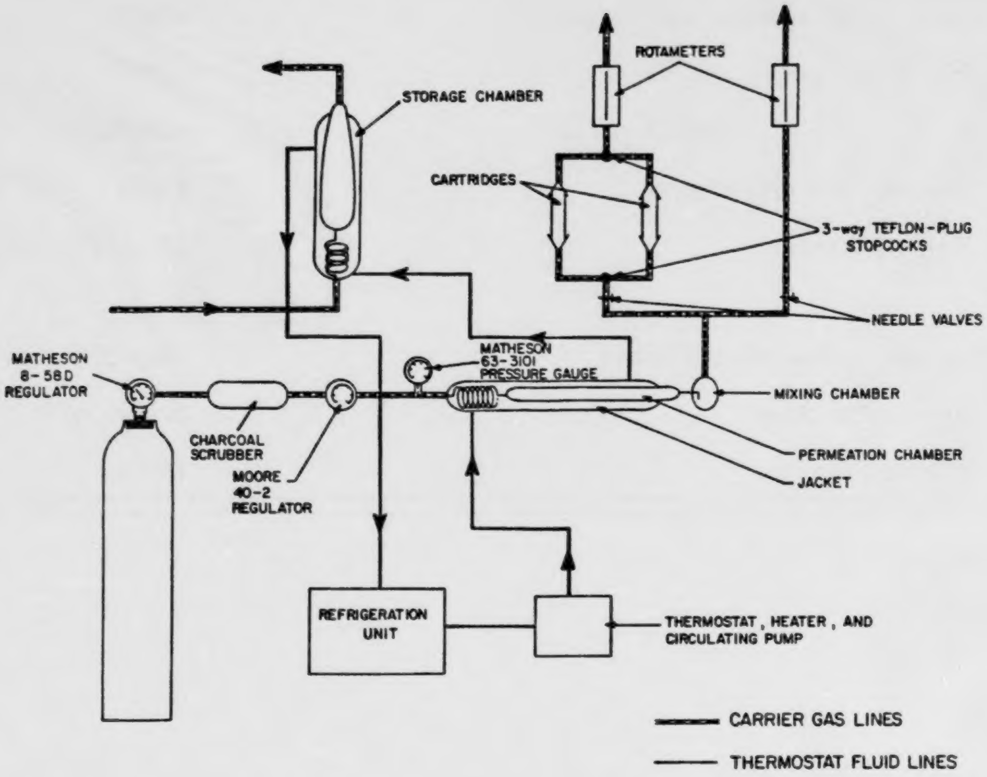

ROTAMETERS
STORAGE CHAMBER
CARTRIDGES
3-way TEFLON-PLUG STOPCOCKS
NEEDLE VALVES
MATHESON 8-58D REGULATOR
MATHESON 63-3101 PRESSURE GAUGE
MIXING CHAMBER
CHARCOAL SCRUBBER
MOORE 40-2 REGULATOR
PERMEATION CHAMBER
JACKET
REFRIGERATION UNIT
THERMOSTAT, HEATER, AND CIRCULATING PUMP
CARRIER GAS LINES
THERMOSTAT FLUID LINES

Figure 6. Permeation system for generating air/vapor mixtures (9,13).

TABLE 2. PERMEATION TUBES FOR SEVERAL VOLATILE PRIORITY POLLUTANTS

Priority pollutant	Permeation tube		Approximate rate g/min
	Dimensions (O.D. x I.D. x length, cm)	Material	
methyl choride	0.64 x 0.48 x 6.5	FEP	1.8×10^{-6}
dichlorodifluoromethane	Unknown		
methylbromide	0.64 x 0.48 x 6.0	FEP	1.2×10^{-6}
vinyl chloride	0.64 x 0.48 x 10.0	FEP	2.0×10^{-6}
chloroethane	Unknown		
dichloromethane	0.64 x 0.48 x 11.0	FEP	7.0×10^{-7}
trichlorofluoromethane	Unknown		
1,1-dichloroethylene	0.64 x 0.48 x 10.1	TFE	1.0×10^{-6}
1,1-dichloroethane	0.64 x 0.48 x 9.9	TFE	4.2×10^{-7}
1,2-*trans*-dichloroethylene	0.64 x 0.48 x 10.0	TFE	1.1×10^{-5}
chloroform	0.64 x 0.48 x 11.0	FEP	6.4×10^{-8}
1,2-dichloroethane	0.64 x 0.48 x 8.0	TFE	4.0×10^{-7}
1,1,1-trichloroethane	0.64 x 0.48 x 8.0	TFE	9.1×10^{-8}
carbon tetrachloride	0.64 x 0.48 x 9.9	TFE	3.0×10^{-8}
bromodichloromethane	0.64 x 0.48 x 5.2	TFE	1.1×10^{-7}
bis-(chloromethyl) ether	Unknown		
1,2-dichloropropane	0.64 x 0.48 x 7.7	TFE	9.8×10^{-8}
1,3-*trans*-dichloropropane	Unknown		
trichloroethylene	0.64 x 0.48 x 10.0	TFE	2.2×10^{-6}
dibromochloromethane	Unknown		
1,3-*cis*-dichloropropene	Unknown		
1,1,2-trichloroethane	0.64 x 0.48 x 10.3	TFE	6.2×10^{-8}
benzene	0.64 x 0.32 x 0.6	PE	7.1×10^{-6}
2-chloroethylvinyl ether	Unknown		
bromoform	0.64 x 0.48 x 5.1	PE	2.5×10^{-5}
1,1,2,2-tetrachloroethene	0.64 x 0.48 x 5.2	TFE	3.6×10^{-7}
1,1,2,2-tetrachloroethane	0.64 x 0.32 x 7.0	PE	9.7×10^{-6}
toluene	0.64 x 0.48 x 7.0	TFE	1.9×10^{-7}
chlorobenzene	0.64 x 0.48 x 5.5	TFE	2.0×10^{-7}
ethyl benzene	0.64 x 0.48 x 12.7	TFE	6.8×10^{-8}
acrolein	0.64 x 0.48 x 10.0	TFE	1.3×10^{-6}
acrylonitrile	0.64 x 0.48 x 10.4	TFE	1.0×10^{-6}
bis-(2-chloroethyl)ether	0.64 x 0.48 x 8.3	TFE	1.0×10^{-10}
perfluorotoluene	0.64 x 0.48 x 7.2	FEP	8.94×10^{-6}
1,3-dichlorobenzene	0.64 x 0.32 x 9.0	PE	1.1×10^{-7}
perfluorobenzene	0.64 x 0.48 x 5.5	FEP	8.5×10^{-6}

from the permeation system. The Tenax GC cartridges were then analyzed immediately, as well as at 14 and 21 days, respectively, using thermal desorption gas-liquid chromatography with flame ionization.

Sample Desiccation

Tenax GC sampling cartridges were loaded with calibrated amounts (400-800 ng/cartridge) of a selected series of priority (purgeable) pollutants and then exposed to a humid atmosphere which was generated by purging a vessel containing water at 40°C. Purging of the Tenax cartridge with humid atmosphere was at 25 ml/min for 5 min.

Tenax GC sampling cartridges which had and had not been exposed to humid atmospheres were analyzed immediately (5 min after humidification) and at 2 hrs, 2, and 3 weeks of storage. In each case, the Tenax GC sampling cartridge was placed in a Kimax® culture tube (Fig. 7) which contained approximately 1 gram of $CaSO_4$. The calcium sulfate had previously been heated in a muffle furnace to 500°C for approximately 4 hr to insure that the calcium sulfate was anhydrous and free of organic volatiles.

All experiments were conducted in duplicate. Tenax sampling cartridges were analyzed by gas-liquid chromatography with flame ionization detection as described above.

RESULTS AND DISCUSSION

Breakthrough Volumes

Table 3 presents the breakthrough volumes for several priority (purgeable) pollutants. The priority pollutants are arranged according to boiling point and divided into halogenated and non-halogenated groups. These data indicate that the boiling point does not always determine the breakthrough volume. For example, the breakthrough volume of 1,2-*trans*-dichloroethylene (1.9 ℓ/cartridge) which has a boiling point of 47.5°C is less than that of dichloromethane (14 ℓ/cartridge). Furthermore, the halogen substitution pattern plays an important role in determining the retention volume on Tenax GC sorbent. The presence of an aromatic substituent also greatly increases the breakthrough volume [compare halogenated compounds with similar boiling points (*e.g.*, chlorobenzene *vs*. 1,1,2,2-tetrachloroethane)].

These data are important for quantitative sampling of air streams. Quantitative data may be obtained for 1,1-dichloroethylene if the sampling volume is less than the breakthrough volume. For example, to estimate the concentration of 1,1,-dichloroethylene in the air stream from the wastewater systems at an ambient temperature of 32.2°C (90°F), a sampling volume of 1 ℓ or less should be taken. This volume (as demonstrated in Section 9) is the desired volume that is required to collect a sufficient quantity of priority pollutant for ppb analysis, while not exceeding the background threshold (resolution requirement) or saturating the instrumental analysis systems.

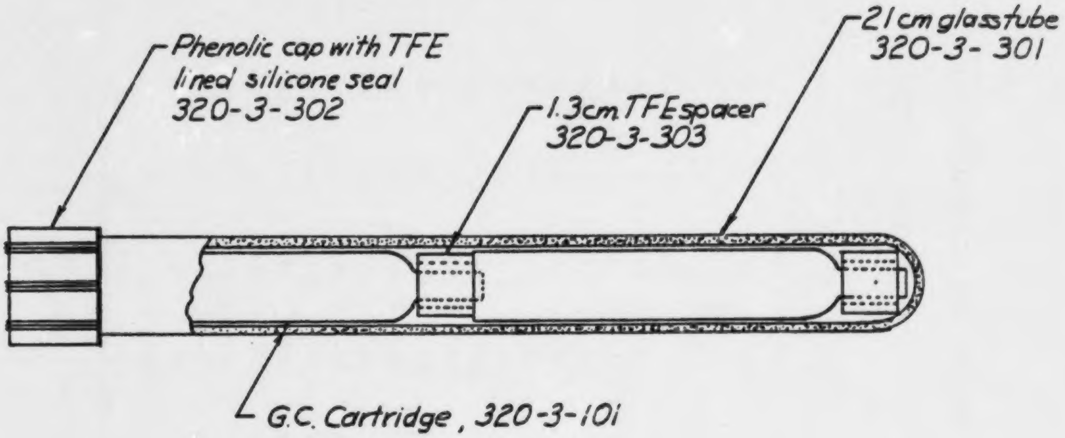

Phenolic cap with TFE lined silicone seal 320-3-302
1.3cm TFE spacer 320-3-303
21 cm glasstube 320-3-301
G.C. Cartridge, 320-3-101

Figure 7. Sampler cartridge transport tube (Nutech Corp., Durham, NC).

TABLE 3. BREAKTHROUGH VOLUMES FOR SEVERAL PRIORITY POLLUTANTS[a]

Priority pollutants	B.P.	Breakthrough Volume										
		Temperature °F (°C)										
		50(10)	55(12.7)	60(15.5)	65(18.3)	70(21.1)	75(23.9)	80(26.7)	85(29.4)	90(32.2)	95(34.9)	100(37.8)
1,1-dichloroethylene	32	2.4	2.2	1.8	1.6	1.4	1.3	1.2	1.1	1.0	0.97	0.87
dichloromethane	40	14	12	9.7	8.3	6.9	5.9	4.9	4.1	3.5	2.9	2.4
1,2-*trans*-dichloroethylene	47.5	1.90	1.81	1.73	1.68	1.65	1.51	1.44	1.38	1.31	1.25	1.20
1,1-dichloroethane	57	8.9	7.9	7.0	6.3	5.6	5.0	4.5	3.9	3.5	3.1	2.7
chloroform	61.2	17	14	12	10	9.1	7.7	6.6	5.6	4.8	4.2	3.5
1,1,1-trichloroethane	74	23	21	18	16	15	14	12	10	9	8	7
carbon tetrachloride	76.8	41	34	29	24	20	17	14	12	10	8	7
1,2-dichloroethane	84	49	42	36	31	27	23	20	17	15	12	11
trichloroethylene	87	90	78	67	58	50	44	38	33	28	24	21
bromodichloromethane	90	83	70	61	52	45	39	34	29	25	22	19
1,2-dichloropropane	96.2	229	199	162	138	115	98	81	69	58	49	41
1,1,2-trichloroethane	113	309	245	208	177	151	128	109	93	79	67	57
tetrachloroethylene	121	361	361	267	250	196	170	144	125	106	92	78
chlorobenzene	132	899	776	653	563	473	408	344	296	249	215	181
1,1,2,2-tetrachloroethane	146	477	406	353	308	262	228	199	173	147	128	112
bromoform	149.5	511	445	388	330	287	245	213	186	158	138	117
1,3-dichlorobenzene	172	2,393	2,075	1,758	1,524	1,291	1,119	948	885	697	603	510
1,4-dichlorobenzene	174	2,390	2,071	1,752	1,520	1,289	1,113	937	812	688	592	497
bis-(2-chloroethyl)ether	178	1,692	1,440	1,226	1,043	888	768	653	560	477	406	354
1,2-dichlorobenzene	179	2,422	2,191	1,960	1,716	1,463	1,301	1,139	989	839	769	699
acrolein	52	1.9	1.8	1.7	1.5	1.4	1.3	1.2	1.1	1.0	0.91	0.83
acrylonitrile	77	8.5	7.4	6.6	5.7	5.0	4.4	3.9	3.4	3.0	2.6	2.3
benzene	80	108	92	77	65	54	46	38	32	27	23	19
toluene	110.6	494	421	348	296	245	209	173	147	122	104	86
ethylbenzene	136	1,393	1,188	984	838	693	590	487	415	344	293	243

[a] Breakthrough volume is in ℓ/cartridge (1.5 cm i.d. x 6.0 cm bed of 35/60 mesh Tenax GC).

The data presented in Table 3 serve as a guideline for selecting the volume which may be sampled at various ambient air temperatures if one wishes to achieve quantitative estimation of priority pollutants.

Sample Storage

Table 4 presents the recovery of priority pollutants from Tenax GC sampling cartridges which were stored for 14 and 21 day periods. These data represent recovery from Tenax sampling cartridges which were loaded with calibrated amounts of priority pollutants under ideal conditions, *i.e.*, in the absence of humidity. As these data indicate, most compounds may be stored adsorbed to Tenax GC for as long as 3 weeks prior to analysis. However, it is recommended that the sampling cartridges be analyzed as soon as possible after sampling has been completed.

Effect of Calcium Sulfate Drying on Recovery of Priority Pollutants from Tenax GC Cartridges

Tables 5, and 6 present the relative recoveries of priority pollutants from Tenax GC cartridges which were humidified and stored for various lengths of time in the presence of $CaSO_4$ to determine the effects of drying on the percent recovery of priority pollutants. It is apparent that, in some cases, the drying step enhances the recovery of the priority pollutants while in other cases some losses are observed. However for the majority of compounds listed, "drying" in the presence of $CaSO_4$ decreases their percent recoveries.

TABLE 4. RECOVERY OF PRIORITY POLLUTANTS FROM STORED TENAX CARTRIDGES

Priority pollutant	Percent recovery	
	14 days	21 days
1,1-dichloroethylene	48 ± 12	35 ± 8
1,2-*trans*-dichloroethylene	73 ± 9	99 ± 12
1,1,1-trichloroethane	92 ± 2	ND[a]
1,2-dichloroethane	100 ± 7	122 ± 9
trichloroethylene	99 ± 9	87 ± 13
1,2-dichloropropane	86 ± 4	ND
tetrachloroethylene	97 ± 3	68 ± 3
chlorobenzene	80 ± 7	87 ± 3
bis-(2-chloroethyl)ether	86 ± 6	93
bis-(chloromethyl)ether	41 ± 4	ND
acrolein	45 ± 15	49 ± 6
acrylonitrile	ND	81 ± 6
benzene	104 ± 8	104
toluene	103 ± 3	103 ± 7
ethylbenzene	61 ± 9	65 ± 11
chlorobenzene	80 ± 7	80 ± 4
1,1-dichloroethane	102	90
bromodichloromethane	106	77
bromoform	79	ND

[a] ND = not determined.

TABLE 5. RELATIVE RECOVERIES OF WET VS. DRIED SAMPLES USING $CaSO_4$ FOR 2 HR

Priority pollutant	Humidified	Humidified, dried	% D/H
benzene	15.4 ± 2.1	13.7 ± 1.3	89
bromodichloromethane	1.6 ± 0.3	1.5 ± 0	94
toluene	49.9	53.8 ± 0.8	110
chlorobenzene	25.9 ± 2.9	31.3 ± 1.1	120
1,2-dichlorobenzene	37.9 ± 24.1	37.9 ± 16.4	100
1,1-dichloroethylene	17.3	25.8	149
1,2-*trans*-dichloroethylene	8.3 ± 1.8	6.0	72
chloroform	2.6 ± 0.5	1.9 ± 0.1	73
ethylene dichloride	6.6 ± 0.4	3.5 ± 0	53
1,2-dichloropropane	7.6 ± 1.1	4.7 ± 0.3	62
1,1,2-trichloroethane	16.4 ± 1.8	8.5 ± 1.5	52
tetrachloroethylene	6.8 ± 0.5	4.6 ± 0.6	68
ethylbenzene	18.5 ± 1.6	11.6 ± 1.6	63
1,1,2,2-tetrachloroethane	16.3 ± 5.3	8.3 ± 1.5	51
bis-(2-chloroethyl)ether	2.6 ± 0.4	0.85 ± 0.3	33
1,3-dichlorobenzene	30.7 ± 0.6	21.7 ± 5.7	70
acrolein	23.8 ± 0.3	24.7 ± 1.7	103
acrylonitrile	15.2 ± 2.5	15.7 ± 0.7	102
trichloroethylene	39.2 ± 3.9	36.7 ± 3.9	94

TABLE 6. RELATIVE RECOVERIES OF WET VS DRIED SAMPLES AS A FUNCTION OF STORAGE TIME

Priority pollutants	3 da			2 wk			3 wk		
	Wet	Dried	% D/W	Wet	Dried	% D/W	Wet	Dried	% D/W
1,1-dichloroethane	8.3 ± 0.6[a]	7.5 ± 0.5	90	27.1 ± 4.3	25.3 ± 1.6	93	11.5 ± 0.1	9.9 ± 2.8	86
1,2-*trans*-dichloroethylene	7.2	6.1	85	3.9 ± 0.1	3.6 ± 0.6	92	15.1 ± 3.1	13.6 ± 2.1	90
chloroform	5.0 ± 2.6	2.2 ± 0.2	44	8.1 ± 0.6	6.9 ± 1.3	85	7.2 ± 0.9	6.9 ± 0.9	96
1,2-dichloroethane	6.5 ± 2.5	5.0 ± 1.0	77	-	-	-	13.9 ± 1.5	10.9 ± 1.7	78
1,1,2-trichloroethane	11.7 ± 2.7	11.2 ± 1.2	96	1.2 ± 0.1	1.2 ± 0.1	100	12.2 ± 0.8	10.3 ± 2.3	84
1,1,2,2-tetrachloroethane	9.3 ± 1.8	7.5 ± 0.5	81	5.9 ± 4.5	3.6 ± 1.2	61	8.5 ± 1.5	6.6 ± 0.1	78
trichloroethylene	24	20.8 ± 0.2	87	20.3 ± 2.3	19.1 ± 1.6	94	22.5	22.3 ± 0.5	99
1,1,1-trichloroethane	7.3	6.2 ± 1.6	85	6.1 ± 1.1	2.3 ± 0	38	6.6	2.0 ± 0.2	30
tetrachloroethylene	6.2 ± 1.2	6.8 ± 0.8	109	14.9	12.7 ± 0.7	85	12.7 ± 2.1	15.1 ± 0.1	118
1,1-dichloroethylene	-	-	-	2.4	2.8	116	-	-	-
bromodichloromethane	3.6 ± 0.5	5.1 ± 0.1	71	8.3 ± 0.3	6.2 ± 0.9	75	-	-	-
1,2-dichloropropane	6.7 ± 0.3	6.9 ± 0.9	102	7.3	5.8 ± 0.4	79	6.7 ± 0.4	7.0 ± 0.4	104
bis-(2-chloroethyl)ether	3.5 ± 1.3	1.8 ± 0.3	51	2.0	1.1 ± 0.1	55	1.7 ± 0.3	1.4 ± 0.3	82
chlorobenzene	-	-	-	34.1 ± 5.4	32.0 ± 2.5	94	36.5 ± 0.3	35.7 ± 2.3	86
1,2-dichlorobenzene	3.5 ± 0.2	3.8 ± 0.3	108	67.0	42.8 ± 7.4	64	12.2 ± 2.6	9.9 ± 2.1	81
1,3-dichlorobenzene	27	30.0 ± 0.9	111	27.9 ± 3.5	21.8 ± 2.2	78	27.6 ± 7.3	29.4 ± 1.0	106
benzene	51.1 ± 0.1	50.8 ± 0.3	99	41.4 ± 6.7	33.7 ± 1.7	81	31.2 ± 1.0	31.2 ± 3.0	100
toluene	-	-	-	70.4 ± 1.2	69	98	-	-	-
ethylbenzene	18.3 ± 3.0	17.8 ± 0.8	97	-	-	-	57 ± 12	55 ± 2.0	98
acrylonitrile	14.5	11.4 ± 0.6	79	-	-	-	8.7	7.8 ± 0.1	90
acrolein	20.1	18.4 ± 3.6	92	10.3	11.2 ± 1.7	108	9.4	8.1 ± 1.8	86

[a] Average of triplicate analysis.

SECTION 6

RECOVERY OF "PURGEABLE" PRIORITY POLLUTANTS FROM AQUEOUS MEDIA

INTRODUCTION

It would be desirable if the levels of priority pollutants which are determined in the air stream passing from wastewaters could be related to their concentration in the original raw or municipal wastewater. Some preliminary studies have been performed in estimating the potential concentrations of priority pollutants which might be found in the air passing through water (14). These studies have considered the mass transfer of vapors between two phases and the Henry's law constant. Using these relationships, calculations have been performed for chloroform as the model compound (14). However, one of the important assumptions of this approach is that the priority pollutants behave as ideal compounds which is necessary when applying Henry's law. One of the factors not taken into consideration in these calculations was the possiblity that the priority pollutants might be adsorbed to the solid phase particles and thus not available for stripping by the air stream.

In order to examine the possibility of whether Henry's law can be applied, a series of experiments was conducted to determine the percent recovery of priority pollutants from distilled water and from raw and municipal wastewater. Comparison of these data would allow the analyst then to ascertain whether an empirical approach is feasible.

EXPERIMENTAL

Distilled Water Experiments

Three vessel configurations were used in the recovery studies of priority pollutants from distilled water (Fig. 8). The first two vessels (Fig. 8) permitted the water to be circulated in a manner similar to aeration ponds at municipal treatment plants. Air was passed through the column of water producing a circular vector motion in the vessel. Two vessels of this design were employed; the basic differences were in their diameter to length ratios. A third vessel (Fig. 8) was also used; however, in this case a sintered glass frit created a fine bubble dispersion of the air stream as it passed into the liquid column.

Standard solutions of the priority pollutants were prepared in methanol and added to distilled water to produce the desired final concentrations. In all cases, the experiments were conducted in duplicate.

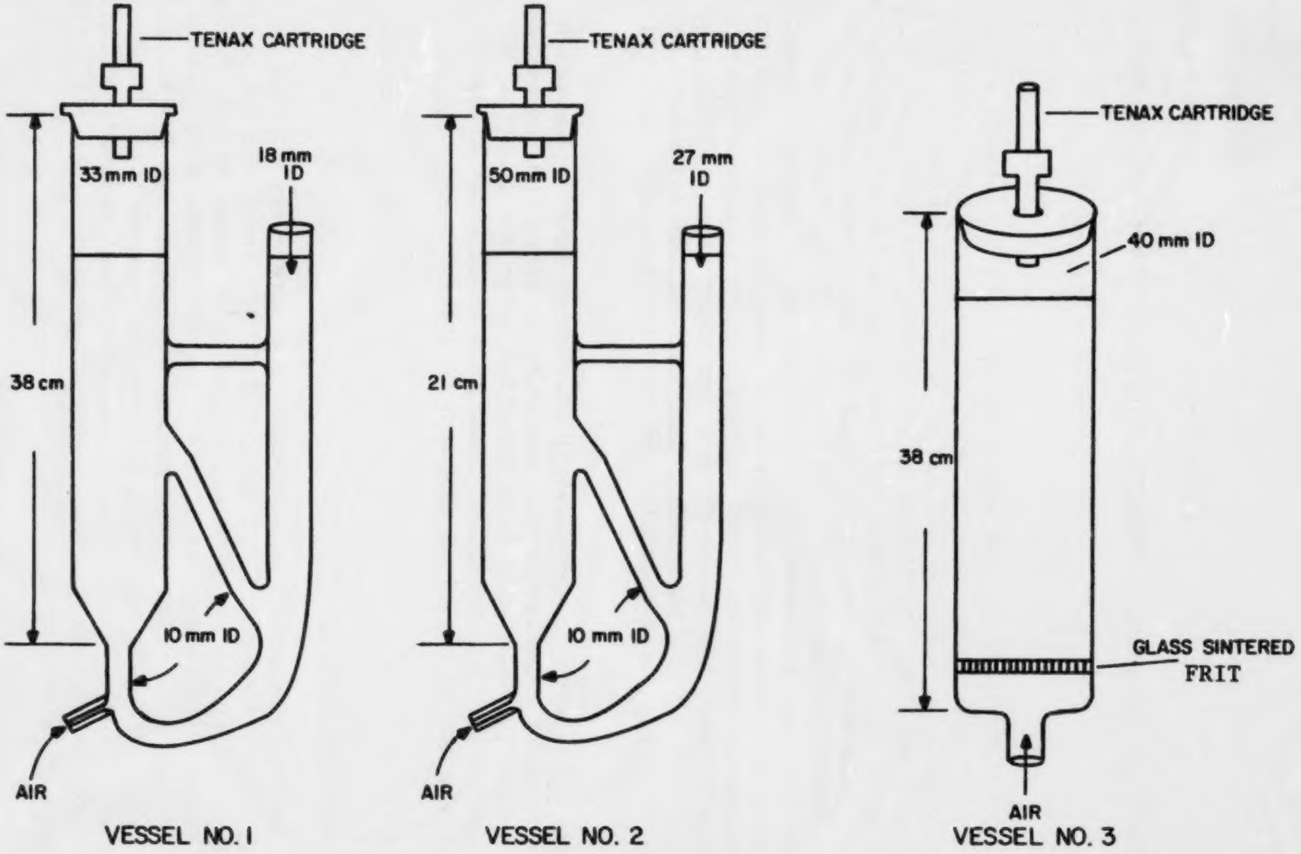

TENAX CARTRIDGE
33mm ID
18 mm ID
38 cm
10 mm ID
AIR
VESSEL NO. 1
TENAX CARTRIDGE
50mm ID
27 mm ID
21 cm
10 mm ID
AIR
VESSEL NO. 2
TENAX CARTRIDGE
40 mm ID
38 cm
GLASS SINTERED FRIT
AIR
VESSEL NO. 3

Figure 8. Vessel configurations employed in air-stripping experiments.

Purging of the air stream through the three vessel types (Fig. 8) was conducted using an air/liquid volume ratio of 2:1. The rate was 80 ml/min. For purposes of comparison, a constant volume (400 ml) was used in all experiments. The air stream passed through a Tenax GC sampling cartridge (1.5 cm x 6.0 cm) which was identical to that used in field experiments. Analysis of these cartridges was performed as described in Section 5 under gas-liquid chromatography.

Methods-of-Addition Studies

Methods-of-addition studies were performed with activated sludge mixed liquor. Increasing measured amounts of priority pollutants were added followed by purging, trapping, and GC/fid analysis. Standard solutions of the priority pollutants were prepared in methanol and added directly to the mixed liquor. An equilibration time of 30 min was used prior to beginning the purge and trap for the priority pollutants.

The purging experiments employed the vessel (Fig. 8) with a glass frit to produce a fine air bubble stream. Four-hundred-ml volumes of mixed liquor were purged in all cases.

Activated sludge from the Durham, NC, Northside Sewage Treatment Plant was used. The experiments were performed at the treatment plant using fresh sludge, since its transport back to the laboratory might have changed the integrity of the sample. Also, for these reasons a short equilibration time was used.

Using 400 ml of activated sludge mixed liquor spiked with varying amounts of priority pollutants, the sample was purged with 800 ml of air at 80 ml/min. The priority pollutants were trapped on a Tenax GC sampling cartridge (1.5-cm i.d. x 6.0-cm bed length) and then analyzed by GC/fid as described under Section 5.

Recovery Studies on Raw Wastewater and Activated Sludge Mixed Liquor

Standards of each priority pollutant were prepared in methanol and added to raw wastewater and activated sludge mixed liquor to produce a final concentration of ∿1 ppb. Vessel configuration No. 3 was used (Fig. 8). Again 800 ml of air was passed through 400 ml wastewater at 80 ml/min. The purge-and-trap technique was identical to that described for the methods of addition experiment. The priority pollutants were collected onto Tenax GC sampling cartridges and analyzed by GC/MS/COMP techniques. All experiments were conducted in triplicate.

Gas Chromatography/Mass Spectrometer/Computer Analysis

A previously described inlet manifold was used for thermally recovering priority pollutants trapped on Tenax GC sampling cartridges and transferring them to a gas chromatograph/mass spectrometer/computer system (5,6,8,9,10,12). This manifold was designed to be used with either packed or support coated open tubular (SCOT) columns if necessary.

A Finnigan Model 3300 GC/MS system equipped with a PDP-12 computer was capable of providing ion chromatograms as well as reporting the absolute intensity or areas of ion peaks. Quantitative data concerning the priority pollutants of interest were based on a ratio of responses between compounds and internal standards. The instrumental conditions used for the analysis of priority pollutants collected on the sorbent Tenax GC sampling cartriges is given in Table 7. The thermal desorption chamber and the six-port Valco valve (Valco Instr., Inc., Houston, TX) were maintained at 270°C. The glass jet separator was maintained at 250°C. The mass spectrometer was set to scan the mass range from 25-300 amu. The helium purge gas through the desorption chamber was adjusted to 15 ml/min. The nickel capillary trap on the inlet manifold was cooled with liquid N_2. In a typical thermal desorption cycle, a sampling cartridge was placed in the preheated desorption chamber and the helium gas was passed through the cartridge to purge the priority pollutant vapors into the liquid nitrogen capillary trap [the inert activity of the trap has been shown in previous studies (9)]. After the desorption was completed, the six-port valve was rotated and the temperature on the capillary loop was raised rapidly (>150°/min). The carrier gas introduced the vapors onto the gas chromatographic column, the gas chromatographic column was held for 3 min at 60°C and then programmed 8°/min to 160°C and held until all compounds were eluted.

A stainless steel tube (8 ft in length x 0.1-in. i.d.) packed with Carbopack C (60/80 mesh) coated with 0.2% Carbowax 1500 preceded by a 1-ft x 0.1-in. i.d. column packed with Chromsorb W coated with 3% Carbowax 1500 was used for effecting the resolution of the volatile priority pollutants (15). The chromatographic column was conditioned for 24 hrs at 220°C with 40 ml/min carrier flow (helium) prior to its use.

The GC/MS/COMP system was calibrated with regard to both mass and intensity/quantity of priority pollutant in order to estimate the priority pollutants on the sampling cartridges. These techniques are described in Section 8.

RESULTS AND DISCUSSION

Distilled Water Studies

Table 8 presents the percent recovery of priority pollutants from deionized-distilled water using three different vessel configurations. For vessel configurations 1 and 2, the air bubble size was approximated at 1.0 cm while for vessel No. 3, the bubble size was ∿0.3 cm. The percent recovery of the priority pollutants from vessel No. 2 was slightly better than from vessel No. 1. In general, the highest recoveries were observed with the vessel utilizing a glass frit for dispersing the air stream as it entered into the liquid. A general trend was observed: those compounds which had lower vapor pressures also subsequently gave lower recoveries. Furthermore, those compounds which were water-soluble were difficult to purge from the aqueous medium (e.g., acrolein and acrylonitrile).

These data indicate that the recovery of priority pollutants from the deionized-distilled water is influenced by the vessel configuration and

TABLE 7. OPERATING PARAMETERS FOR GC-MS-COMP SYSTEM

Parameter	Setting
Inlet-manifold[a]	
desorption chamber and valve	270°C
capillary trap - trap cycle	-195°C
inject cycle	+250°C
thermal desorption time	8 min
He purge rate	15 ml/min
GC	
column	60-160°C, 8°/min
He carrier flow	40 ml/min
GC/MS interface (glass jet separator, transfer line)	250°C
MS[b]	
scan range	*m/z* 25→300
scan cycle rate, automatic cyclic	∿2 sec
emission current	500 μA
electron energy	70 eV
ion energy	6 v
lens voltage	-100 v
extractor voltage	8 v
samples/amu	1

[a] Available from Nutech Corp., Durham, NC.

[b] Conditions for quadrupole instrument.

TABLE 8. PERCENT RECOVERY OF PRIORITY POLLUTANTS FROM DEIONIZED/DISTILLED WATER FOR THREE VESSEL CONFIGURATIONS

Priority pollutant	Vessel-1	Vessel-2	Vessel-3
1,1-dichloroethylene	ND[a]	82[b]	67
1,2-*trans*-dichloroethylene	59 ± 13[c]	96 ± 7	103 ± 2
1,1-dichloroethane	86 ± 19	94 ± 5	98 ± 1
chloroform	77 ± 22	88 ± 14	87 ± 7
1,1,1-trichloroethane	ND	91	ND
carbon tetrachloride	93 ± 5	83 ± 11	80 ± 9
1,2-dichloroethane	79 ± 7	84 ± 4	83 ± 7
trichloroethylene	81 ± 4	104 ± 6	109 ± 20
bromodichloromethane	116 ± 8	ND	90 ± 1
1,2-dichloropropane	84 ± 8	66 ± 20	94 ± 16
1,1,2-trichloroethane	63 ± 17	63 ± 4	72 ± 12
tetrachloroethylene	64 ± 29	65 ± 17	86 ± 7
chlorobenzene	69 ± 13	106 ± 3	102 ± 4
1,1,2,2-tetrachloroethane	55 ± 7	58 ± 2	60 ± 3
bromoform	68 ± 11	85 ± 7	87 ± 8
1,3-dichlorobenzene	36 ± 5	59 ± 29	67 ± 24
bis-(2-chloroethyl)ether	77 ± 20	72 ± 18	64 ± 3
1,2-dichlorobenzene	33 ± 2	47 ± 13	69 ± 2
acrolein	40 ± 5	41 ± 3	36 ± 3
acrylonitrile	37 ± 4	37 ± 9	42 ± 11
benzene	115 ± 27	ND	103 ± 8
toluene	55	51	60

[a] ND = not determined.

[b] Single value.

[c] Average of triplicate determinations.

possibly by air bubble size. Since aeration of wastewater treatment basins is conducted under many different conditions, it is difficult to relate the percent air stripping of priority pollutants from an aqueous medium to a particular set of conditions.

Methods-of-Addition Studies

Table 9 presents the results of the method-of-addition study for priority pollutants in raw wastewater at the Durham, NC, Northside Treatment Plant. The quantity of the priority pollutant added was in the ppb range. The results are expressed in arbitrary units of detector response (peak height or area). Where indicated, the data represent triplicate analyses. Figures 9-12 present linear regressions for the methods-of-addition study on this raw wastewater. As indicated in these figures, many of the compounds gave linear regressions with x-y intercepts below zero. This indicates possible sorption of the priority pollutants to organic solids. For some pollutants a positive intercept was observed, and later GC/MS/COMP results confirmed their presence in the original raw wastewater. These data clearly indicate that, for the priority pollutants examined and even though a linear response was observed, the priority pollutants are not recovered in a predictable fashion. These observations suggest that it is difficult to extrapolate from air stream concentrations to the concentrations in the raw wastewater using percent recoveries.

The methods-of-addition study indicated substantial quantities of chlorobenzene, trichloroethylene, bromodichloromethane and 1,3-dichlorobenzene to be present in the original raw wastewater.

Table 10 presents data for priority pollutants in activated sludge at the Durham, NC, treatment plant. Where indicated, the analyses were performed in triplicate. Figures 13-17 present the linear regression analyses for the method-of-addition study on activated sludge. Trends similar to those observed in the raw wastewater occurred. Even though a linear response was observed, the x-y intercept was not zero, but was instead negative, indicating the loss of compounds which were added to the sludge (probably by sorption to the sludge or by degradation to other compounds). A positive x-y intercept occurred too, suggesting that the priority pollutant was in the original municipal wastewater. Because the methods of addition experiments were conducted at different times, it was not possible to compare the concentrations for the raw wastewater and activated sludge.

Percent Recovery of Priority Pollutants from Raw Wastewaters and Activated Sludge

A series of experiments was conducted in order to ascertain the percent recovery of priority (purgeable) pollutants at the ppb level from raw wastewater and activated sludge from different wastewater treatment plants. Table 11 presents the results for raw wastewater. In general the recoveries decreased as the levels of the added priority pollutants decreased. The highest recoveries were observed for bromodichloromethane (80%), trichloroethylene (82%) and bromoform (71%), when added at 40 ppb. As might be expected, the interpretation of these data is complicated by the fact that

TABLE 9. METHODS-OF-ADDITION STUDY FOR PRIORITY POLLUTANTS FROM RAW WASTEWATER

Priority pollutant	Quantity added (ppb) 160	120	80	40
dichloromethane	417[a]	379	-	117 ± 33
1,2-*trans*-dichloroethylene	1,187	944 ± 128[b]	305 ± 25	140 ± 18
1,1-dichloroethane	1,374	1,800	707 ± 3	304 ± 110
chloroform	477 ± 69	-	191 ± 14	134 ± 12
1,1,1-trichloroethane	147 ± 3	122 ± 50	102 ± 1	-
carbon tetrachloride	854 ± 129	691	-	138 ± 2
1,2-dichloroethane	323 ± 7	276	65 ± 1.4	57 ± 1.3
trichloroethylene	1,062 ± 184	907 ± 313	507 ± 101	309 ± 66
bromodichloromethane	516	455	253 ± 3	153 ± 34
1,2-dichloropropane	799 ± 312	590	-	174 ± 21
1,1,2-trichloroethane	251 ± 49	204	111 ± 6	76 ± 6
tetrachloroethylene	1,961 ± 101	1,545	567 ± 11	389 ± 3
chlorobenzene	3,225	2,997	2,689 ± 110	-
bromoform	3,715	2,478	-	723 ± 131
1,3-dichlorobenzene	2,594 ± 80	2,063 ± 218	1,717	-
1,2-dichlorobenzene	23,840	16,717	-	-
acrolein	I	I[d]	I	I
acrylonitrile	1,252 ± 664	679 ± 291	374 ± 65	186 ± 13
benzene	7,068	5,254	2,750	1,447 ± 440
toluene	5,310	4,594	2,545 ± 18	1,228 ± 225
ethylbenzene	4,640 ± 46	3,811	-	1,349 ± 252

[a] Single value, arbitrary units.

[b] Average of triplicate determinations.

[c] Not determined.

[d] Interferents.

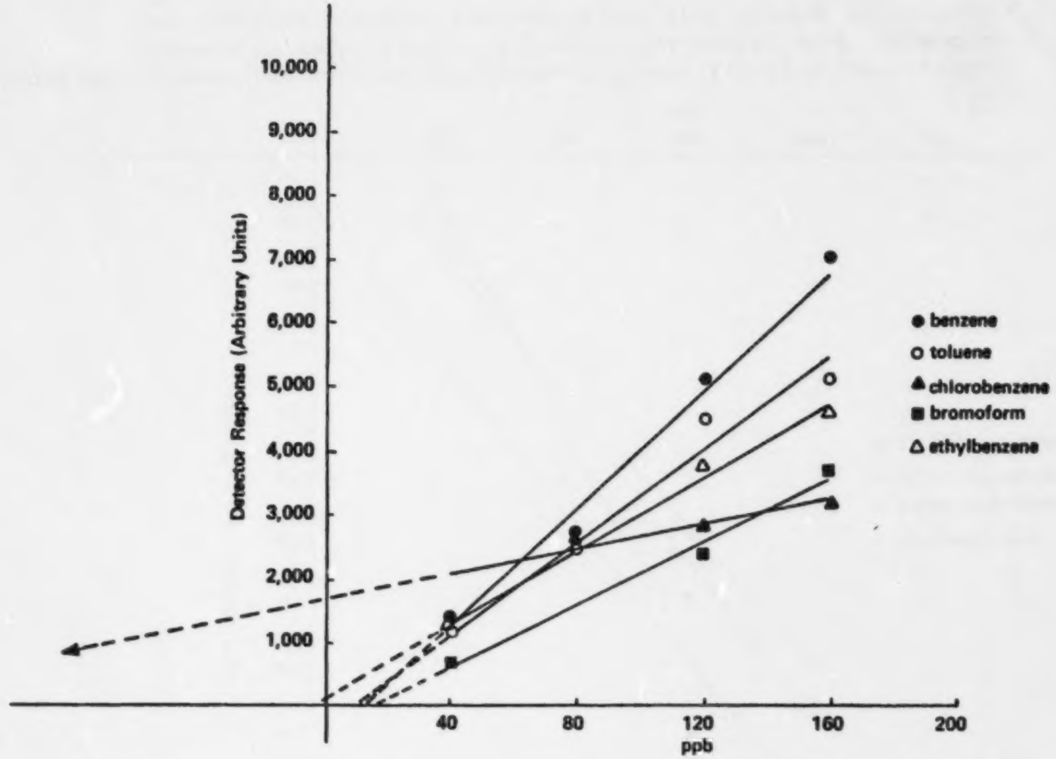


Figure 9. Linear regressions (benzene, toluene, chlorobenzene, bromoform ethylbenzene) for methods-of-addition study on raw wastewater from Durham, NC, Northside Treatment plant.

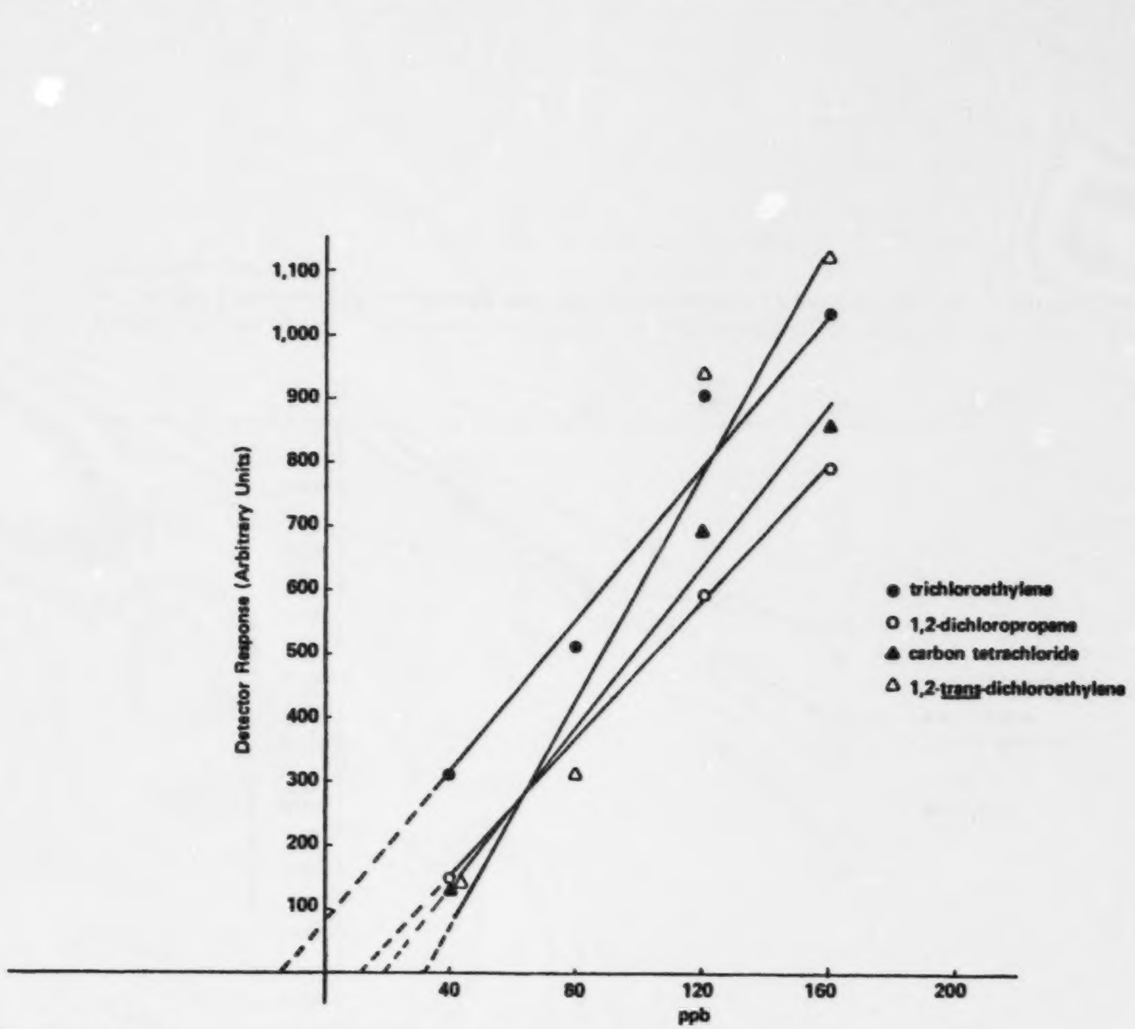


Figure 10. Linear regressions (trichloroethylene, 1,2-dichloropropane, carbon tetrachloride, 1,2-*trans*-dichloroethylene) for methods-of-addition study on raw wastewater from Durham, NC Northside Treatment plant.

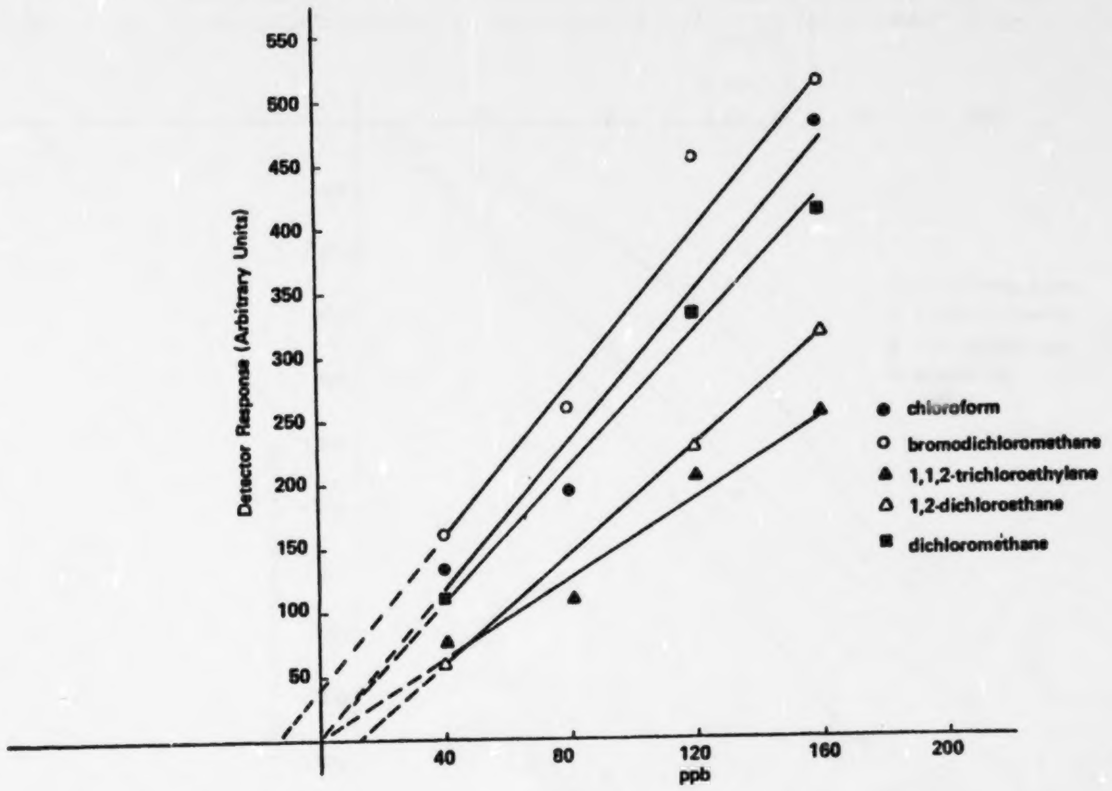


Figure 11. Linear regressions (chloroform, bromodichloromethane, 1,1,2-trichloroethylene, 1,2-dichloroethane, dichloromethane) for methods-of-addition study on raw wastewater from Durham, NC, Northside Treatment plant.

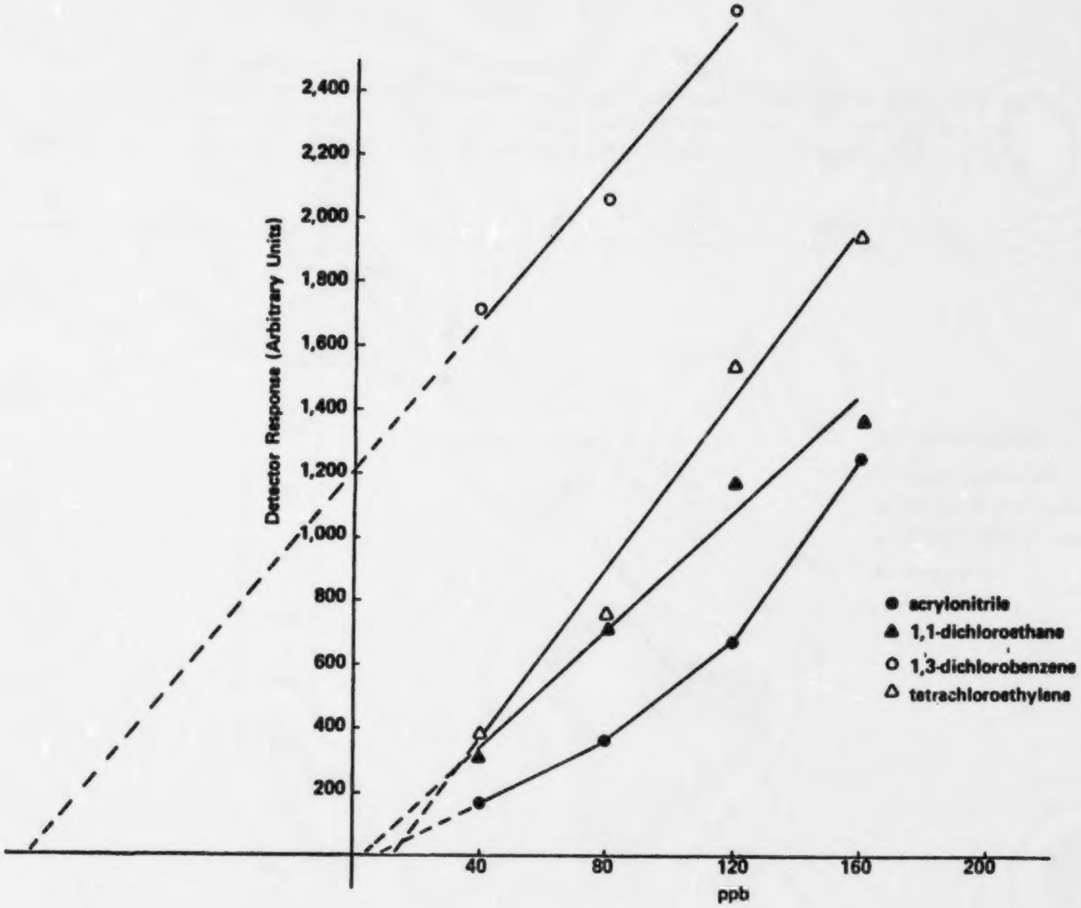


Figure 12. Linear regressions (acrylonitrile, 1,1-dichloroethane, 1,3-dichlorobenzene, tetrachloroethylene) for methods-of=addition study on raw wastewater from Durham, NC, Northside Treatment plant.

TABLE 10. METHODS-OF-ADDITION STUDY FOR PRIORITY POLLUTANTS FROM ACTIVATED SLUDGE

Priority pollutant	Quantity added (ppb) 200	160	150	120	100	80	50	40
1,1-dichloroethylene	-[a]	36 ± 13[b]	-	24 ± 1.4	-	I	-	I
dichloromethane	11.3 ± 1.3	-	-	-	5.1 ± 0.1	-	1.9 ± 0.5	-
1,2-*trans*-dichloroethylene	-	847 ± 102	-	746 ± 78	-	593	-	-
1,1-dichloroethane	47 ± 7	-	-	-	23 ± 1	-	7.4	-
chloroform	-	435 ± 36	-	327 ± 46	-	-	-	151
1,1,1-trichloroethane	-	147 ± 3	-	122	-	102 ± 1	-	I
carbon tetrachloride	-	396 ± 44	-	276	-	159	-	-
1,2-dichloroethane	-	274 ± 32	-	229 ± 41	-	143	-	107
trichloroethylene	-	1,062 ± 184	-	907 ± 313	-	507 ± 100	-	309 ± 67
bromodichloromethane	9.7 ± 0.4	-	8.4 ± 0	-	5.7 ± 0.5	-	2.2 ± 0.6	-
1,2-dichloropropane	-	732 ± 30	-	566 ± 75	-	391	-	285
1,1,2-trichloroethane	-	279 ± 9	-	231 ± 39	-	188	-	135
tetrachloroethylene	-	842 ± 2	-	599 ± 45	-	469	-	226
chlorobenzene	58 ± 1.2	-	49[d]	-	35 ± 3	-	17 ± 2.2	-
bromoform	3.4 ± 0.1	-	2.6 ± 0.1	-	1.8 ± 0.2	-	0.7 ± 0.2	-
1,3-dichlorobenzene	-	1,558 ± 105	-	1,206 ± 109	-	-	-	606
1,2-dichlorobenzene	25 ± 0.5	-	20	-	15 ± 1.7	-	7.2 ± 0.4	-
acrolein	-	I[c]	-	I	-	I	-	I
acrylonitrile	-	1,252 ± 664	-	679 ± 291	-	374 ± 65	-	186 ± 3
benzene	111	-	-	-	72	-	22	-
toluene	93 ± 3.3	-	-	-	59	-	28 ± 4.4	-
ethylbenzene	-	2,521 ± 77	-	1,824 ± 179	-	1,272	-	-

[a] Not determined.

[b] Average of triplicate determinations, arbitrary units.

[c] Interferent.

[d] Single value.

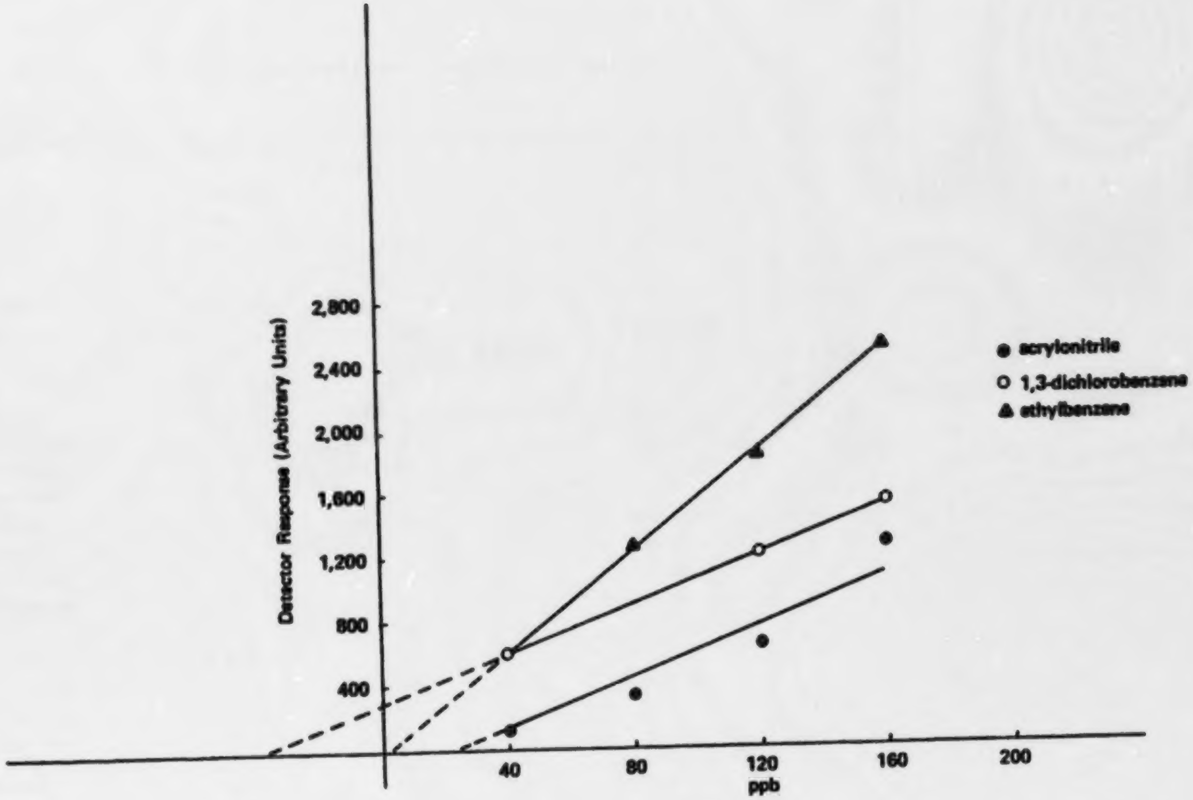


Figure 13. Linear regressions (acrylonitrile, 1,3-dichlorobenzene, ethylbenzene) for methods-of-addition study on activated sludge from Durham, NC, Northside Treatment plant.

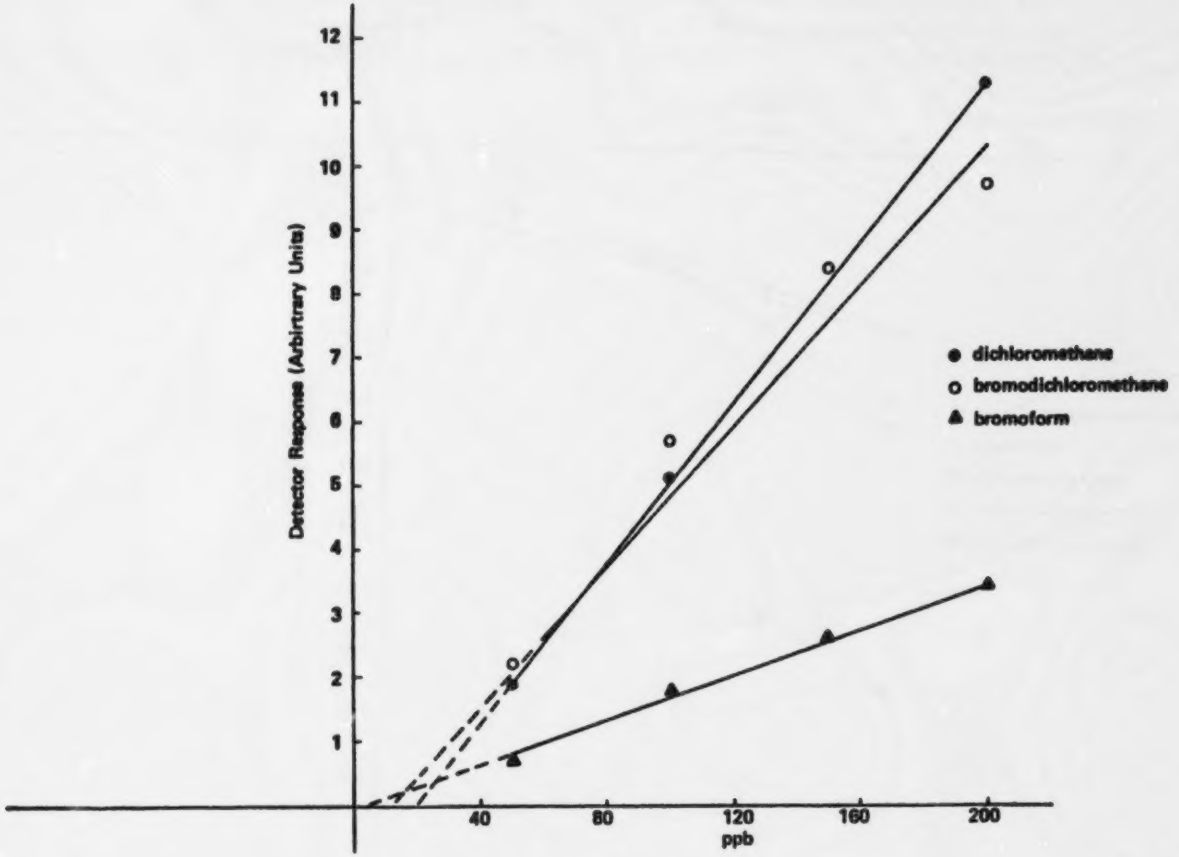


Figure 14. Linear regressions (dichloromethane, bromodichloromethane, bromoform) for methods-of-addition study on activated sludge from Durham, NC Northside Treatment plant.

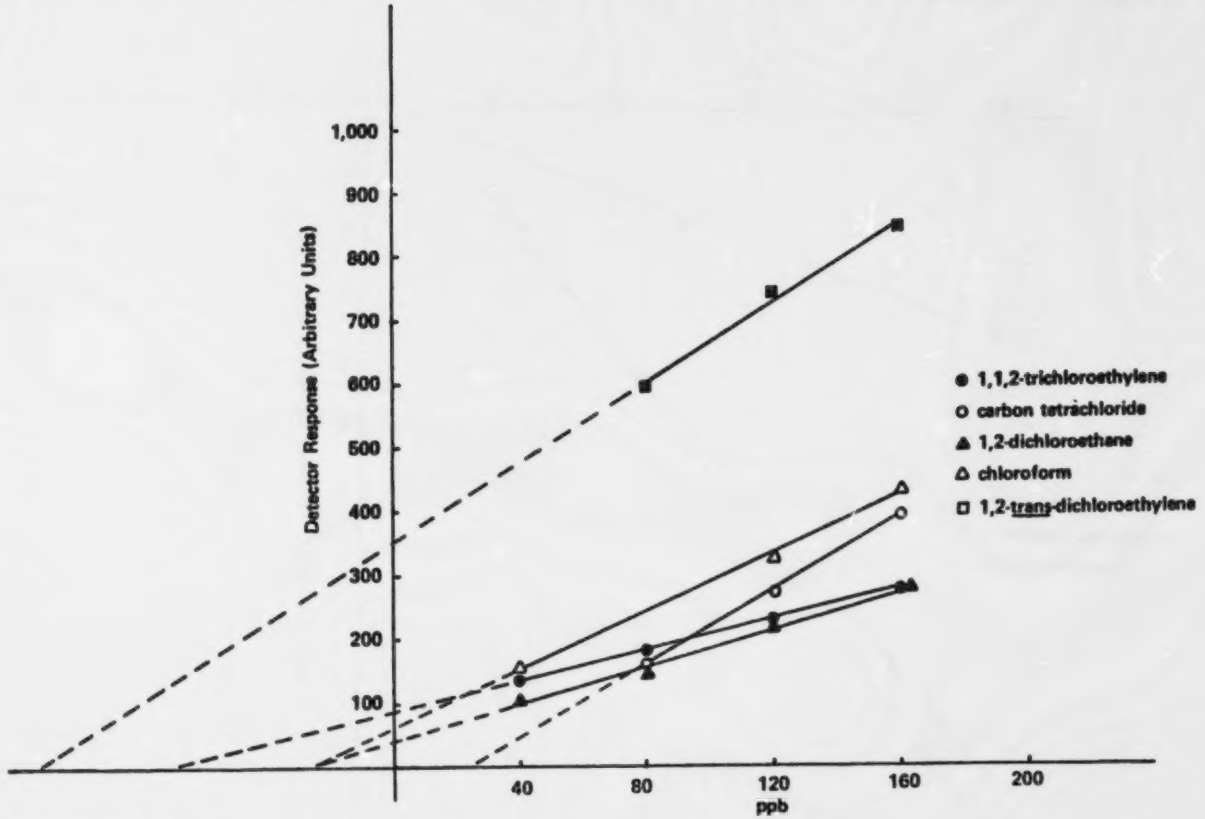


Figure 15. Linear regressions (1,1,2-trichloroethylene, carbon tetrachloride, 1,2-dichloroethane, chloroform, 1,2-*trans*-dichloroethylene) for methods-of-addition study on activated sludge from Durham, NC Northside Treatment plant.

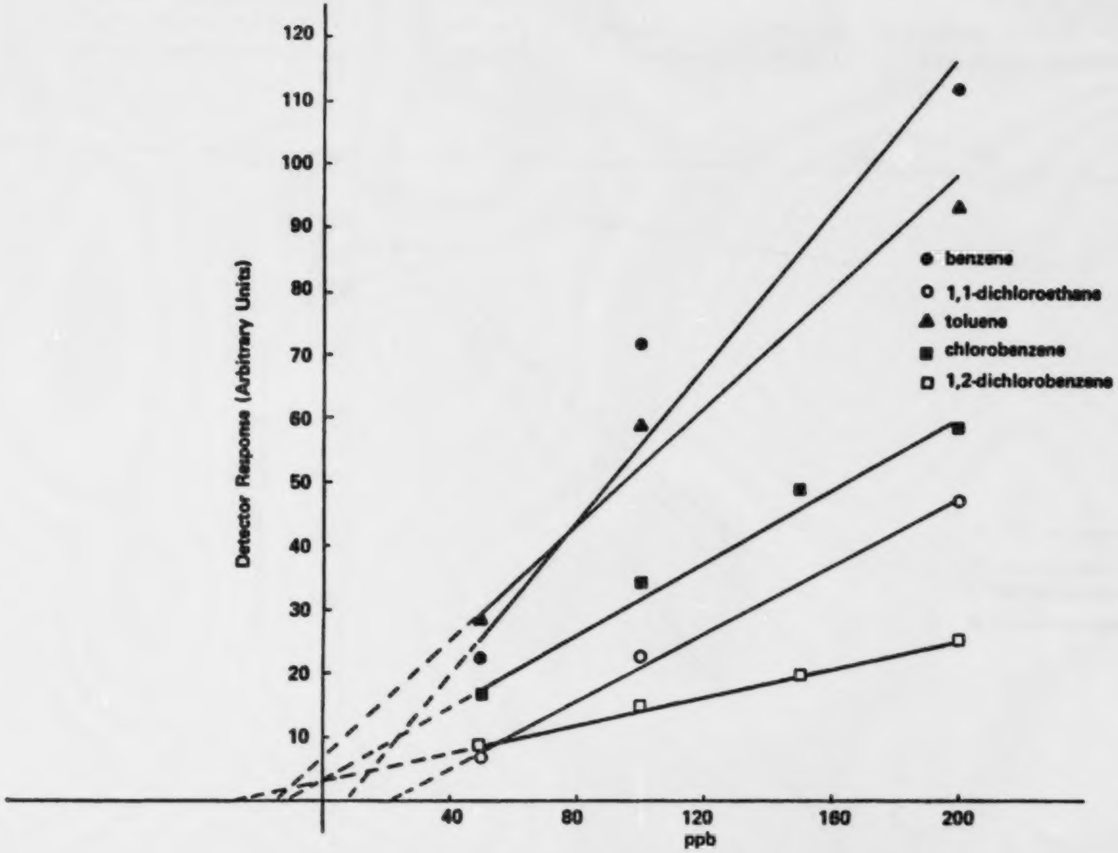


Figure 16. Linear regressions (benzene, 1,1-dichloroethane, toluene, chlorobenzene, 1,2-dichlorobenzene) for methods-of-addition study on activated sludge from Durham, NC Northside Treatment plant.

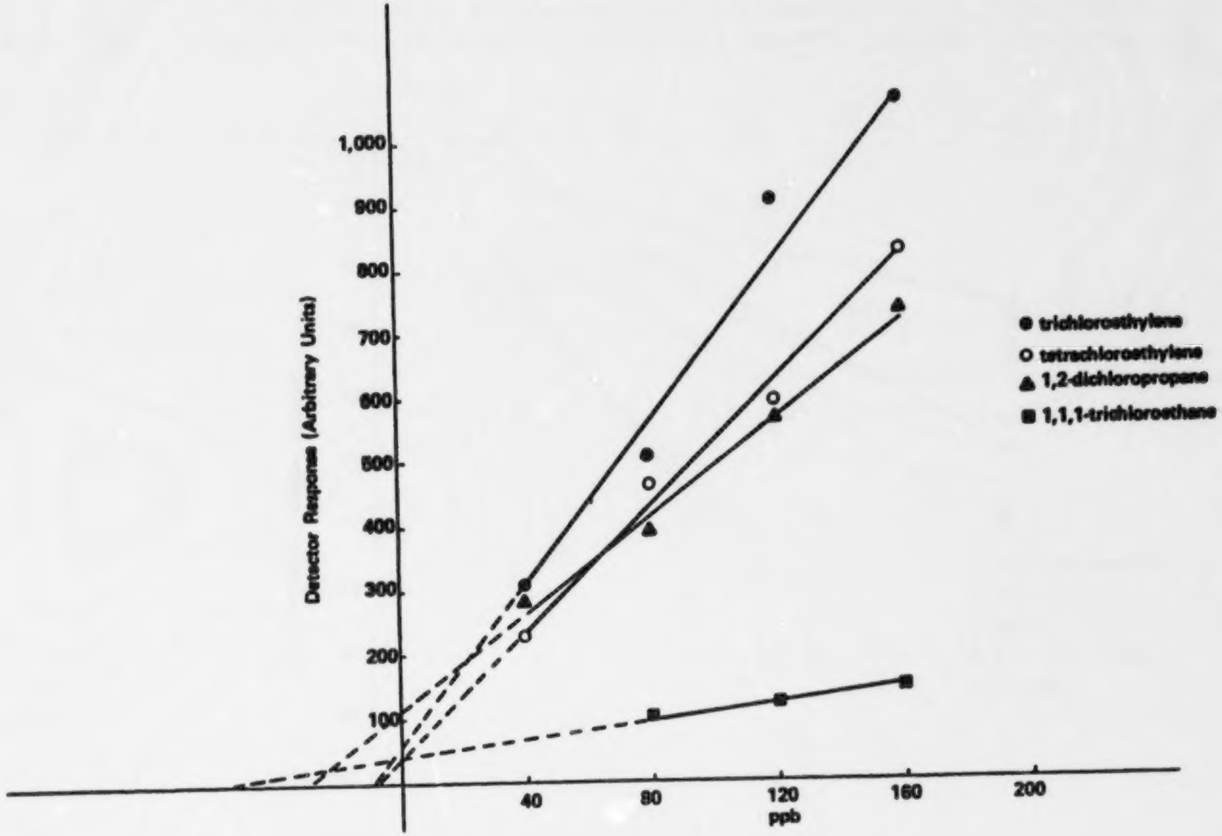


Figure 17. Linear regressions (trichloroethylene, tetrachloroethylene, 1,2-dichloropropane, 1,1,1-trichloroethane) for methods-of-addition study on activated sludge from Durham, NC Northside Treatment plant.

TABLE 11. PERCENT RECOVERY OF PRIORITY POLLUTANTS FROM RAW WASTEWATER FROM GRIT CHAMBER AT DURHAM WASTE TREATMENT PLANT

	Percent recovery			
Priority pollutant	160 ppb	120 ppb	80 ppb	40 ppb
1,2-*trans*-dichloroethylene	92[a]	98 ± 13[b]	47 ± 4	44 ± 6
1,1-dichloroethane	42	60	43 ± 1	37 ± 10
chloroform	18 ± 3	-[c]	14 ± 1	30 ± 3
1,1,1-trichloroethane	15 ± 1	17 ± 7	21 ± 1	-
carbon tetrachloride	26 ± 4	34	-	21 ± 1
1,2-dichloroethane	9 ± 1	10	4 ± 1	6 ± 1
trichloroethylene	71 ± 12	78 ± 30	64 ± 13	82 ± 17
bromodichloromethane	69	82	68 ± 1	80 ± 18
1,2-dichloropropane	16 ± 6	16	-	15 ± 2
1,1,2-trichloroethane	30 ± 6	34	42 ± 3	38 ± 2
tetrachloroethylene	71 ± 4	76	40 ± 1	56 ± 1
chlorobenzene	30	38	51 ± 2	-
bromoform	87	82	-	71 ± 13
1,3-dichlorobenzene	28 ± 1	28 ± 3	37	-
1,2-dichlorobenzene	30	31	36	25 ± 4
acrolein	I[d]	I	I	I
acrylonitrile	45 ± 23	23 ± 14	27 ± 5	27 ± 2
benzene	34	34	26	28 ± 8
toluene	25	29	24 ± 1	23 ± 23
ethylbenzene	8 ± 1	9	-	10 ± 2

[a] Single value.

[b] Average of triplicate determinations.

[c] Not determined.

[d] Interferents.

the raw wastewater in some cases already contained the priority pollutant of interest. The lowest recovery was observed for ethyl benzene at approximately 10%.

Table 12 gives the percent recovery from activated sludge. As might be expected, in general these recoveries are considerably lower than those for the raw wastewater. The data in Tables 11 and 12 correspond to the methods of addition study which was presented earlier.

Tables 13-15 give additional recovery studies which were conducted on raw wastewater and activated sludge from the South Burlington, NC, wastewater treatment plant and from the Chapel Hill, NC, plant. In contrast, these experiments were conducted at the 1 ppb level. A high degree of variability can be expected in the percent recovery of priority pollutants from raw wastewater and activated sludge. For these reasons and for reasons cited earlier, it is virtually impossible to accurately predict (±2%) the concentrations of priority pollutants in the raw wastewater or activated sludge based on their level in the air stream.

TABLE 12. PERCENT RECOVERY OF PRIORITY POLLUTANTS FROM ACTIVATED SLUDGE AT DURHAM WASTE TREATMENT PLANT

Priority pollutant	Quantity added (ppb)							
	200	160	150	120	100	80	50	40
1,1-dichloroethylene	-	53 ± 19[a]	-[b]	50 ± 3	-	I	-	I
1,2-*trans*-dichloroethylene	-	90 ± 11	-	93 ± 10	-	96	-	-
1,1-dichloroethane								
chloroform	-	59 ± 5	-	45 ± 6	-	-	-	65
1,1,1-trichloroethane	-	15 ± 1	-	17	-	22 ± 1	-	I
carbon tetrachloride	-	12 ± 1	-	11		10	-	-
1,2-dichloroethane	-	7 ± 1	-	8 ± 1	-	7	-	12
trichloroethylene	-	50 ± 9	-	59 ± 20	-	57 ± 14	-	63 ± 13
bromodichloromethane	44 ± 3	-	51 ± 0	-	50 ± 2	-	50 ± 14	-
1,2-dichloropropane	-	16 ± 1	-	14 ± 2	-	13	-	14
1,1,2-trichloroethane	-	32 ± 2	-	35 ± 6	-	43	-	40
tetrachloroethylene	-	62 ± 1	-	59 ± 4	-	60	-	57
chlorobenzene	18 ± 1	-	20	-	21 ± 2	-	20 ± 1	-
bromoform	42 ± 1	-	41 ± 4	-	39 ± 4	-	37 ± 10	-
1,3-dichlorobenzene	-	17 ± 1	-	17 ± 2	-	-	-	39
1,2-dichlorobenzene	19 ± 1	-	18	-	19 ± 2	-	17 ± 1	-
acrolein	-	I	-	I[c]	-	I	-	I
acrylonitrile	-	37 ± 19	-	34 ± 14	-	45 ± 8	-	22 ± 1
benzene	20[d]	-	-	-	25	-	16	-
toluene	13 ± 1	-	-	-	19	-	18 ± 3	-
ethylbenzene	-	5 ± 0	-	4 ± 0	-	5	-	-

[a] Average of triplicate determinations.

[b] Not determined.

[c] Interferent.

[d] Single value.

TABLE 13. RECOVERY OF PRIORITY POLLUTANTS FROM RAW WASTEWATER FROM GRIT CHAMBER AT SOUTH BURLINGTON, NC WASTEWATER TREATMENT PLANT

Priority pollutant	ng/cartridge	ppb (observed)[a]	% recovery
dichloromethane	91 ± 21[b]	0.23 ± 0.05	23 ± 5
1,1-dichloroethylene	131 ± 27	0.33 ± 0.07	33 ± 7
acrylonitrile	ND[c]	ND	0
1,2-*trans*-dichloroethylene	44 ± 19	0.11 ± 0.05	11 ± 5
1,2-dichloroethane	251 ± 71	0.63 ± 0.18	63 ± 18
carbon tetrachloride	106 ± 45	0.27 ± 0.11	27 ± 11
bromodichloromethane	160 ± 34	0.40 ± 0.08	40 ± 8
benzene	214 ± 23	0.53 ± 0.05	53 ± 5
bromoform	208 ± 47	0.52 ± 0.12	52 ± 12
chlorobenzene	120 ± 13	0.30 ± 0.03	30 ± 3
1,2-dichlorobenzene	156	0.04	40

[a] Spiked at 1 ppb.

[b] Average of triplicate determinations.

[c] ND = not detected.

TABLE 14. RECOVERY OF PRIORITY POLLUTANTS FROM ACTIVATED SLUDGE FROM SOUTH BURLINGTON, NC WASTEWATER TREATMENT PLANT

Priority pollutant	ng/cartridge	ppb (observed)[a]	% recovery
dichloromethane	174 ± 3[b]	0.44 ± 0	44 ± 0
1,1-dichloroethylene	15 ± 0.8	0.04 ± 0	4 ± 0
acrylonitrile	ND[c]	ND	0
1,2-*trans*-dichloroethylene	ND	ND	0
chloroform	ND	ND	0
1,2-dichloroethane	175 ± 44	0.44 ± 0.11	44 ± 11
1,1,1-trichloroethane	214 ± 13	0.54 ± 0.03	54 ± 3
carbon tetrachloride	47 ± 12	0.12 ± 0.03	12 ± 3
bromodichloromethane	67 ± 0.5	0.17 ± 0	17 ± 0
benzene	134 ± 13	0.33 ± 0.03	33 ± 3
trichloroethylene	244 ± 13	0.61 ± 0.08	61 ± 8
bromoform	79 ± 9	0.20 ± 0.03	20 ± 3
tetrachloroethylene	527 ± 145	1.31 ± 0.36	131 ± 36
toluene	314 ± 28	0.78 ± 0.07	78 ± 7
ethylbenzene	295 ± 33	0.74 ± 0.08	74 ± 8
chlorobenzene	78 ± 8	0.19 ± 0.02	19 ± 2
1,2-dichlorobenzene	179 ± 2	0.45 ± 0	45 ± 0

[a] Spiked at 1 ppb.

[b] Average of triplicate determinations.

[c] ND = not detected.

TABLE 15. RECOVERY OF PRIORITY POLLUTANTS FROM RAW WASTEWATER FROM GRIT CHAMBER AT CHAPEL HILL, NC MUNICIPAL WASTE TREATMENT PLANT

Priority pollutant	ng/cartridge	ppb (observed)[a]	% recovery
1,1-dichloroethylene	236 ± 38[b]	0.59 ± 0.09	59 ± 9
1,2-*trans*-dichloroethylene	196 ± 26	0.49 ± 0.06	49 ± 6
1,2-dichloroethane	329 ± 49	0.82 ± 0.12	82 ± 12
bromodichloromethane	271 ± 5	0.68 ± 0.02	68 ± 2
1,2-dichloropropane	170 ± 5	0.43 ± 0.08	43 ± 8
bromoform	256 ± 5	0.64 ± 0.02	64 ± 2
chlorobenzene	235[c]	0.59	59
1,2-dichlorobenzene	278 ± 48	0.69 ± 0.12	69 ± 12

[a] Spiked at 1 ppb.

[b] Average of triplicate determinations.

[c] Single value.

SECTION 7

DESIGN AND FABRICATION OF SAMPLING SYSTEM FOR PRIORITY POLLUTANTS EMITTED FROM MUNICIPAL TREATMENT FACILITIES

INTRODUCTION AND DESIGN CRITERIA

The sampling unit (Fig. 18) was designed for accurate sampling of purgeable organic priority pollutants in municipal sewage treatment facilities. Primary use of this unit is for sampling gaseous evolution from aeration tanks, although with minor modification it can also be used in other areas such as the grit chamber.

The aeration tank may be considered a surface source of non-homogeneous character where the rate of gas evolution as well as the concentration of organics varies from point to point. Time dependence and other variability may also be expected. Obtaining meaningful data under these conditions requires that the total volume of gas evolving from the surface be determined. The sampling head (Fig. 19) must therefore define a certain surface area and channel all gases emitted through the appropriate flow monitors. A skirt extending into the liquid defines the source area and provides the low pressure buildup necessary to force the gas through the sampler. Initially a pressure head allowance of 2 in. of H_2O was provided. This was adequate to handle a flow rate through the sampler of up to 30 ℓ/min. However, after field testing the unit, an additional 4 in. was added to the skirt because of surface turbulence that was encountered. The lower limit on the flow rate was determined by the amount necessary to assure that enough gas would be flowing through the system to use three cartridges simultaneously. Based on considerations described elsewhere, this lower flow limit with a design safety factor would be about 1 ℓ/min. For air-volume to liquid-volume ratios for typical aeration tanks, a surface area of 1 ft^2 should evolve a gas flow within the range of 1 to 30 ℓ/min. The sampling head was made long and narrow instead of square to provide a degree of integration for the variation of emission from center to side of a typical tank.

It was anticipated that turbulence and foaming on the surface would cause non-gaseous material to be carried into the sampling system. Consequently a baffle system was designed to change the direction of flow, raise the air velocity, and provide liquid impingement and runoff. This system was adequate for the situations that were encountered in the field testing program.

The gaseous sample encountered in this situation is saturated with water vapor. To prevent condensation, the sample line is heated to 40°C.

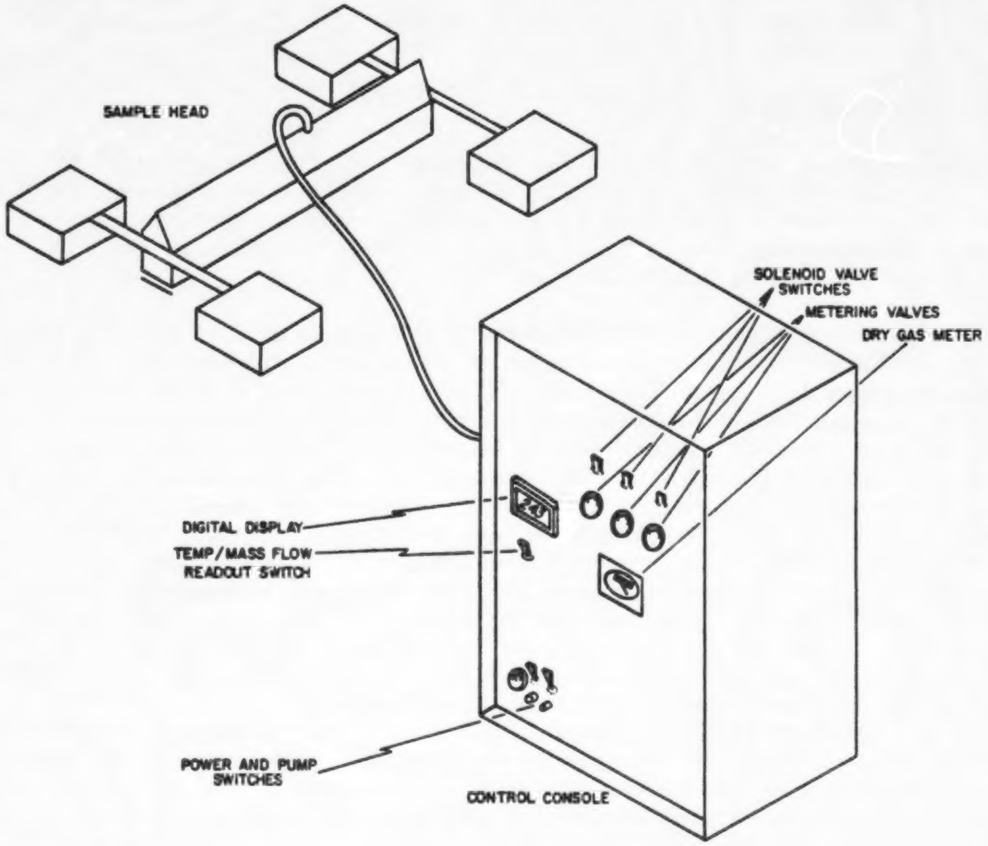
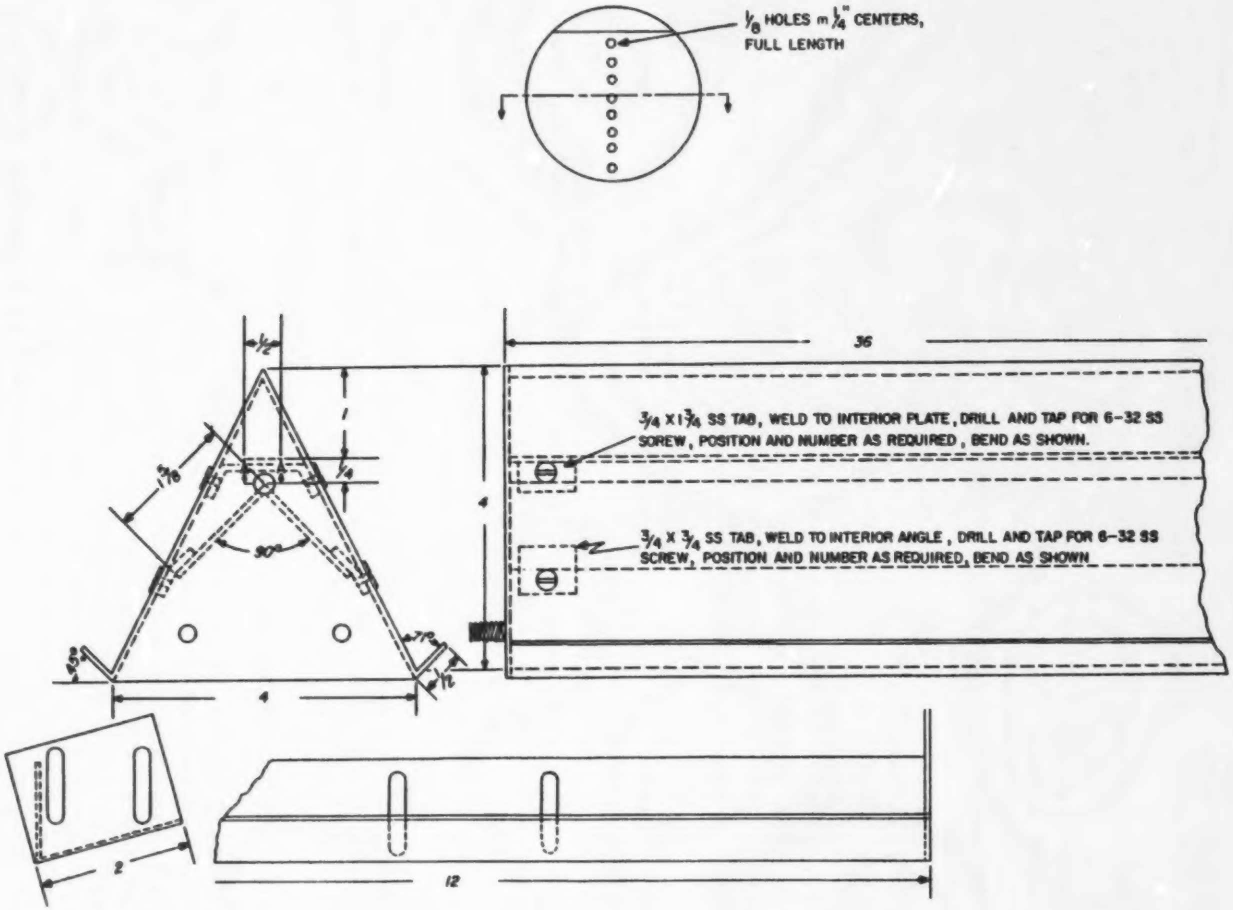

SAMPLE HEAD
SOLENOID VALVE SWITCHES
METERING VALVES
DRY GAS METER
DIGITAL DISPLAY
TEMP/MASS FLOW READOUT SWITCH
POWER AND PUMP SWITCHES
CONTROL CONSOLE

Figure 18. Schematic of sampler system for grit chambers and aeration tanks.



1/8 HOLES on 1/4" CENTERS, FULL LENGTH
3/4 X 1 3/4 SS TAB, WELD TO INTERIOR PLATE, DRILL AND TAP FOR 6-32 SS SCREW, POSITION AND NUMBER AS REQUIRED, BEND AS SHOWN.
3/4 X 3/4 SS TAB, WELD TO INTERIOR ANGLE, DRILL AND TAP FOR 6-32 SS SCREW, POSITION AND NUMBER AS REQUIRED, BEND AS SHOWN
36
1/2
1
1/4
4
90°
4
1/2
2
12

Figure 19. Schematic of sampling shroud.

This temperature prevents condensation and at the same time is not hot enough to cause decomposition and loss of pollutants. Likewise the sample manifold is held at the same temperature. Although breakthrough volumes are lower than at ambient temperature, it would not be desirable to condense moisture in the cartridges. The remainder of the system relies on the residual heat of the gas to maintain it above the dew point.

Pre-cartridge sample contact areas are stainless steel or TFE® to maintain sample integrity. The sample transfer line from the sample head to the console is heated to prevent condensation at low ambient temperatures. In the console samples are collected on three Tenax cartridges--also protected in a temperature-controlled chamber to prevent condensation and to maintain cartridge efficiency during ambient temperature changes during the sampling period.

Sample line temperature and mass flow through the cartridges can be read on a digital display for accurate data logging. Excess gas flow from the sample head that is not diverted through the cartridges is registered on a dry gas meter. Three metering valves adjust the flow through the cartridges. One or more of the flow rates through the cartridges can be monitored without changing flow settings on the mass flow meter by switching activated solenoid valves to individual cartridges.

The stainless steel fabrication of the sample head is also necessary to resist corrosion. It was designed to sample precisely a 1 ft^2 area (Fig. 19). Gas bubbles rising near but not within the defined sample area are deflected by a submerged skirt and flanges. Water is prevented from entering the sample collection line by baffles inside the head and four polyethylene-foam flotation pads provide proper submersion of the skirt and stability in heavy bubble activity.

OPERATION

Operation of the system for sampling aeration tanks can be described in three phases: equipment placement and preparation, set-up for proper flow, cartridge installation and sampling.

Equipment Placement and Preparation

The initial step in this procedure was selecting an appropriate location for the sample head and console. Since tank design and operation vary considerably, care must be exercised to place the units where sufficient bubble activity is present and where the console and sample head can be located within a few feet of each other (the sample line between the head and console is short to maintain accuracy) and within reach of AC power. The sample head can be secured in location by attaching the support arm to a railing. Additional stability can be obtained by attaching ropes to eye bolts located at the ends of the sample head.

Bubble flow rates vary considerably from site to site; however, under typical aeration rates, flow is in the range of 2.5 ℓ/min/ft^2 surface area. The rate can be determined by passing total flow through the dry gas meter for a short period of time, about 10 minutes. During this period the umbilical line and cartridge chamber should stabilize to temperature.

Flow Calibration

Flow through individual cartridge holders was set by adjustment of the metering valves (Fig. 20). With the pump switch on, the solenoid valve corresponding to the holder of interest on, and the digital panel meter switch in the "Mass Flow" position, the metering valve was slowly opened until the mass flow indication reached the desired level. This procedure was repeated for each of the cartridge holders to establish flow through each holder.

When flow rates have been set to the desired level, the solenoid valves could be shut off without disturbing flow settings, and prepared cartridges can be installed for sampling.

Temperature/Mass Flow Readout

The front panel digital display (Fig. 18) can be switched to read either mass flow or umbilical (transfer line) temperature. In the mass flow position the display reads directly in ml/minute; however, in the temperature position the display reads deviation from set point in degrees centigrade.

Temperature Controls

The umbilical temperature was maintained (factory set) at 40°C by a proportional solid state electronic temperature controller (Fig. 21). The set point was adjustable by screw driver on the printed circuit card but it should not require resetting under normal operating conditions. Cartridge chamber temperature is maintained by a self-contained controller/heater and is not adjustable.

SPECIFICATIONS AND COMPONENTS

Power:	115 VAC, 50/60Hz, 5A
Weight:	Control Console - 55 lbs (25 kg) Sample Head - 28 lbs (12.7 kg)
Dimensions:	Control Console - 62 cm H x 40 cm W x 27 cm D Sample Head - 20 cm H x 117 cm W x 81 cm D
Vacuum Pump:	0.5 scfm @ 23 in. Hg
Mass Flow Measurement:	0 - 500 cm^3/min
Dry Gas Meter:	100 cubic meter total, readable to 0.0001 m^3.

Table 16 lists the components for the sampler, and Figures 18-21 depict schematics of the sampling system.

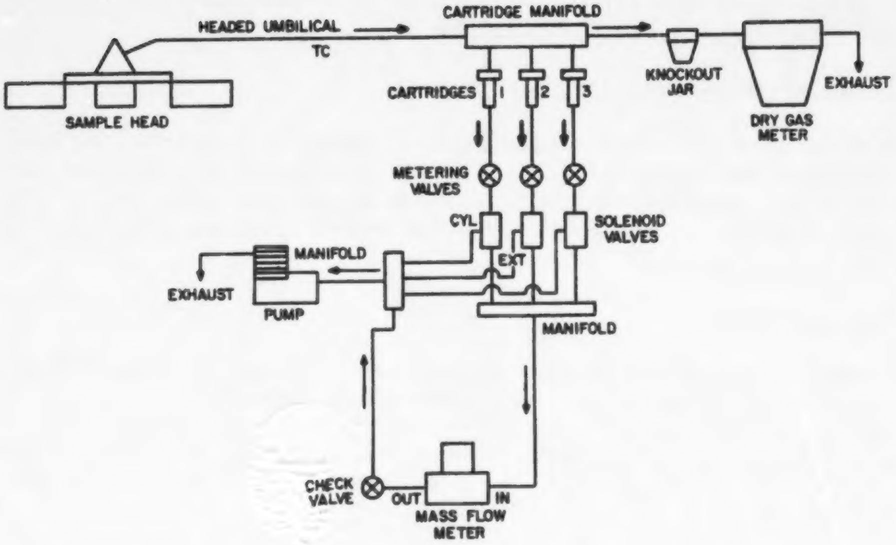

HEADED UMBILICAL
CARTRIDGE MANIFOLD
TC
CARTRIDGES
1
2
3
KNOCKOUT JAR
DRY GAS METER
EXHAUST
SAMPLE HEAD
METERING VALVES
CYL
SOLENOID VALVES
EXT
MANIFOLD
EXHAUST
PUMP
MANIFOLD
CHECK VALVE
OUT
IN
MASS FLOW METER

Figure 20. Diagram of pneumatics in sampler system.

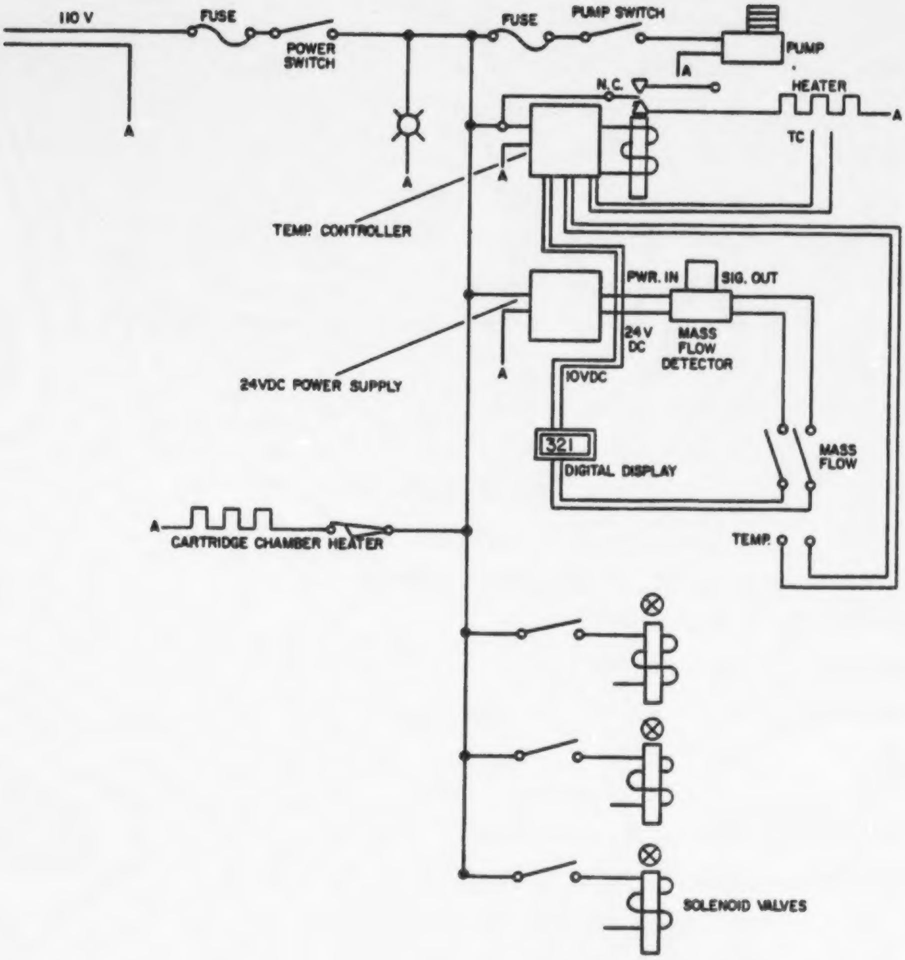

110 V
FUSE
POWER SWITCH
A
FUSE
PUMP SWITCH
PUMP
A
N.C.
HEATER
A
TC
A
A
TEMP. CONTROLLER
PWR. IN
SIG. OUT
24V DC
MASS FLOW DETECTOR
24VDC POWER SUPPLY
A
10VDC
321
DIGITAL DISPLAY
MASS FLOW
A
CARTRIDGE CHAMBER HEATER
TEMP.
SOLENOID VALVES

Figure 21. Schematic of electronics in sampler system.

TABLE 16. PARTS LIST FOR AERATION TANK SAMPLER

Nutech part #[a]	Description	Quantity
851-001	cabinet enclosure #201-002	1
851-002	sample chamber #320-001	1
851-003	stainless sample hood	1
851-004	polyethylene foam pad	4
851-005	heated TFE sample line	1
851-006	quick connect, 1/2" female	1
851-007	quick connect, 1/2" male	1
851-008	thermocouple, type K	1
851-009	dry gas meter w/thermometer installed #221-028	1
851-010	mass flow meter	1
851-011	24 VDC power supply	1
851-012	diaphragm pump	1
851-013	temperature control board	1
851-014	relay w/socket, 110 VAC, DP	1
851-015	4-terminal barrier strip	2
851-016	switch, SPST	2
851-017	fuse holder	2
851-018	LCD display	1
851-019	power cord	1
851-020	male AC connector	1
851-021	female AC connector	1
851-022	switch, DPDT	1
851-023	valve, flow control	3
851-024	valve, solenoid, 110 VAC	3
851-025	stainless manifold, 4 port	1
851-026	stainless manifold, 5 port	1
851-027	check valve	1
851-028	cartridge assembly w/TFE union	3
851-029	sample manifold, 3 port TFE	1
851-030	1/4 NPT nipple, TFE	3

(continued)

TABLE 16 (cont'd.)

Nutech part #[a]	Description	Quantity
851-031	bulkhead union, 1/4"	3
851-032	stainless L	3
851-033	TFE reducer, 1/2" x 7/16"	1
851-034	hose clamp, 7/16"	1
851-035	switch, SPST	3
851-036	indicator lamp	1
851-037	1" foam insulation	2 ft^2
851-038	piano hinge, 8"	1
851-039	deleted	
851-040	screws, misc.	
851-041	house coupling, 1/2 NPT	17
851-042	pot, 1K, 20T	1
851-043	resistor 1%, 8.2K	1
851-044	thermocouple connector, male, type K	1
851-045	thermocouple connector, female, type K	1
851-046	thermocouple connector, mounting bracket	1
851-047	fuse, 2A	1
851-048	fuse, 3A	1
851-049	crimp terminal	30
851-050	vinyl tubing, 3/16 x 5/16"	15 ft
851-051	vinyl tubing, 7/16 x 5/8"	3 ft
851-052	cabinet base #201-001	1
851-053	control panel #201-004	1
851-054	cabinet handles #201-008	3
851-055	knockout jar	1

[a] or its equivalent.

SECTION 8

INSTRUMENTAL (GC/MS/COMP) METHODS OF ANALYSIS

INTRODUCTION

As part of the overall methodology development for collection and analysis of "purgeable" priority pollutants emitted from municipal treatment facilities, it was necessary to delineate the instrumental methods to be used. Under Section 9.0 the previously reported (15) methods for analysis of priority pollutants in industrial effluents using gas chromatograpy/mass spectrometer/computer (GC/MS/COMP) were applied. The purpose of this study was to further define these methods and operating parameters.

The results presented in Section 9.0 indicated that the previously reported techniques were compatible with the analysis of purgeable priority pollutants occurring in the air streams from municipal treatment facilities. This section addresses the method of quantification and detection limits for priority pollutants on Tenax GC sampling cartridges.

EXPERIMENTAL

Instrumental Parameters (GC/MS/COMP)

A Finnigan 3300 GC/MS with a PDP-12 computer was used for defining the instrumental operating parameters.

Instrumental Conditions--

For the analysis of priority pollutants collected on Tenax GC the operating parameters given in Table 17 were used. The thermal desorption chamber and the six-port Valco valve were maintained at 270°C. The glass jet separator was at 250°C. The mass spectrometer was set to scan from 25-300 amu. The helium purge gas through the desorption chamber was 15 ml/min. The nickel capillary trap on the inlet manifold was cooled with liquid N_2. In a typical thermal desorption cycle, a sampling cartridge was placed in a preheated desorption chamber and the helium gas was passed through the cartridge to purge the vapors into the liquid-N_2-cooled trap. After desorption was completed (8 min), the six-port valve was rotated and the temperature on the capillary loop was raised rapidly (>150°/min). Carrier gas then transferred the vapors onto the gas chromatographic column. The chromatographic column was held for 3 min at 60°C, programmed 8°/min to 160°C and, held until all compounds were eluted. The chromatographic column used here was previously described (see Section 5).

TABLE 17. OPERATING PARAMETERS FOR GC-MS-COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber and valve	270°C
capillary trap - trap cycle	-195°C
inject cycle	+250°C
thermal desorption time	8 min
He purge rate	15 ml/min
GC	
column	60-160°C, 8°/min
He carrier flow	40 ml/min
GC/MS interface (glass jet separator, transfer line)	250°C
MS[a]	
scan range	*m/z* 25→300
scan cycle rate, automatic-cyclic	∿2 sec
emission current	500 μA
electron energy	70 eV
ion energy	6 v
lens voltage	-100 v
extractor voltage	8 v
samples/amu	1

[a] Conditions for quadrupole instrument.

Operation of the GC/MS/COMP System--

Typically the mass spectrometer was first set to operate in the repetitive scanning mode. In this mode, the quadrupole automatically scanned upward from a preset low mass to a high mass value. The scan was completed in ∿1 sec. At this time the instrument automatically reset itself to the low mass position in preparation for the next scan, and the information was accumulated by an on-line dedicated computer (PDP-12) and written onto a disk. The scan-plus-reset period was ∿2 sec/scan cycle and was repetitively executed throughout the chromatographic run. Thus data were accumulated as a continuous series of mass spectra throughout the chromatographic run.

The system was calibrated daily by introducing the standard substance heptacosafluorotributylamine and determining the time of appearance of known standard peaks in relation to the scanning field. The calibration curve thus generated was stored in the computer memory. This calibration served only to assign masses over the scanning range.

With the instrument continuously scanning, the sample was then injected and automatic data acquisition was initiated. Upon completion of the chromatographic run, ∿800-1400 spectra accumulated on the disk could be transferred to magnetic tape which was subsequently processed. Depending on the information required that day, data were either processed immediately or additional samples were run, the data were stored on magnetic tape, and the results were examined at a later time.

The mass spectral data were processed in the following manner. First the original spectra were scanned, and integrated ion current information was extracted. The reconstructed ion current profile was then plotted against time on an electrostatic recorder. The information generally indicated whether the run was suitable for further processing since it provided some idea of the number of unknowns in the sample and the resolution obtained using the particular GC column conditions.

Detection Limits--

Using the characteristic ions given in Tables 18, the detection limits for a number of pure authentic priority pollutants loaded onto Tenax GC sampling cartridges were determined by executing the entire process of thermal desorption, gas chromatography and mass spectrometric detection. Standards of the priority pollutants were loaded onto the Tenax GC sampling cartridges using a previously described permeation system (see Section 5). This process involved the repetitive injection of decreasing amounts of each of the priority pollutants and estimation of the limit of detection based on ca a 4:1 signal-to-noise level. The limit of detection therefore is not the quantifiable limit.

Relative Molar Response (RMR) Factors--

Quantification was achieved using standards which were loaded onto the Tenax GC sampling cartriges prior to instrumental analysis by means of the permeation line described earlier and using a unique mass-cracking ion in the mass spectrum of the external standard. In order to eliminate the need to obtain complete calibration curves for each priority pollutant for which quantitative information was desired, the method of relative molar response

(RMR) factors was used (8,13). Successful use of this method requires information on the exact amount of standard added and the relationship of $RMR_{(unknown)}$ to the $RMR_{(standards)}$. The method of calculation is as follows:

$$(1)\quad RMR_{unknown/standard} = \frac{A_{unk}/Moles_{unk}}{A_{std}/Moles_{std}}$$

A = m/z peak area, determined by integration or triangulation.

The value of RMR is determined from at least three independent analyses.

$$(2)\quad RMR_{unk/std} = \frac{A_{unk}/g_{unk}/GMW_{unk}}{A_{std}/g_{std}/GMW_{std}}$$

A = m/z peak area, as above
g = number of grams present
GMW = gram molecular weight

Thus, in the sample analyzed:

$$(3)\quad g_{unk} = \frac{A_{unk} \cdot GMW_{unk} \cdot g_{std}}{A_{std} \cdot GMW_{std} \cdot RMR_{unk/std}}$$

Upon acquiring full spectra throughout the chromatographic run, selected ions were presented as mass fragmentograms using computer software programs which allow the representation of ion intensity vs. time (Table 18). The RMR and quantity of priority pollutant in the samples were estimated using this technique.

RESULTS AND DISCUSSION

Table 19 presents the results of the limit of detection (LOD) study for a series of priority pollutants. The range was approximately from 0.1 ng to 50 ng. These detection limits were determined for the ion given in this table.

Table 20 presents the relative molar response factors which were determined for several priority pollutants using the indicated selected m/z ions. The data represent an average of triplicate determinations. In general, the reproducibility is within 10%. The RMR factors were redetermined approximately 3 weeks later, and these data were within ±20% of the values given in Table 20. Thus it was concluded that during the routine analysis of many samples, cartridges containing calibrated amounts of priority pollutants should be incorporated into the sample set at a frequency which constitutes ∿10% of the sample load. In this manner, relative molar response factors can be generated over a period of time and used to account for variations in the GC/MS/COMP instrumentation (e.g., changes in high-low mass sensitivity with ion source contamination).

TABLE 18. CHARACTERISTIC M/Z IONS SELECTED FOR QUANTIFICATION OF PRIORITY POLLUTANTS

Priority pollutant	M.W.	1st Ion	2nd Ion	3rd Ion
		m/z[a] (I)[b]	m/z[a] (I)[b]	m/z[a] (I)[b]
chloromethane	50.5	50(100)	52(33)	-
dichlorodifluoromethane	120.9	101(13)	103(9)	87(33)
bromomethane	95.0	94(100)	86(94)	-
vinyl chloride	62.5	62(100)	64(33)	-
chloroethane	64.5	64(100)	66(33)	-
dichloromethane	84.9	84(86)	86(55)	49(100)
trichlorofluoromethane	137.4	101(100)	103(66)	-
1,1-dichloroethylene	97	86(80)	93(53)	61(100)
1,1-dichloroethane	99	63(100)	65(33)	83(13)
1,2-*trans*-dichloroethylene	97	96(90)	61(100)	98(57)
chloroform	119.4	83(100)	85(66)	-
1,2-dichloroethane	99	98(23)	100(15)	62(100)
1,1,1-trichloroethane	133.4	97(100)	99(66)	-
carbon tetrachloride	153.8	117(100)	119(96)	121(30)
bromodichloromethane	163.9	127(13)	129(17)	85(66)
bis-(chloromethyl)ether	115.0	79(100)	81(33)	-
1,2-dichloropropane	113	112(4)	114(3)	65(33)
trans-1,3-dichloropropene	113	75(100)	77(33)	-
trichloroethylene	113.4	130(90)	132(85)	97(66)
dibromochloromethane	208.3	127(78)	208(13)	206(10)
cis-1,3-dichloropropene		75(100)	77(33)	-
1,1,2-trichloroethane	113.4	97(100)	99(63)	132(9)
benzene	78.1	78(100)	79(6)	-
2-chloroethylvinyl ether	106.6	106(18)	63(95)	-
bromoform	252.8	173(100)	175(50)	252(11)
1,1,2,2-tetrachloroethylene	165.8	165(78)	166(100)	129(64)
1,1,2,2-tetrachloroethane	167.9	168(6)	137(7)	133(7)
toluene	92.1	91(100)	92(78)	-
chlorobenzene	112.6	112(100)	114(33)	-

(continued)

TABLE 18 (cont'd.)

Priority pollutant	M.W.	1st Ion m/z (I)	2nd Ion m/z (I)	3rd Ion m/z (I)
ethylbenzene	106.2	106(33)	91(100)	-
acrolein	56.1	56(83)	55(65)	-
acrylonitrile	53	53(99)	52(75)	51(32)
perfluorobenzene	186	186(100)	-	-
perfluorotoluene	235	186(100)	263(100)	117(13)
1,2-dichlorobenzene		146(100)	150(10)	-
1,3-dichlorobenzene		146(100)	150(11)	-

[a] Mass to charge ratio

[b] Ion intensity, percent

TABLE 19. ESTIMATED LIMITS OF DETECTION FOR SELECTED PRIORITY POLLUTANTS

Compound	Ion used to quantify	R.T., min (EPA)	R.T., min (RTI)	LOD, ng
chloromethane	50	2.40	-	-
dichlorodifluoromethane	101	2.38	-	-
bromomethane	94	2.50	2.00	5
vinyl chloride	62	2.57	-	-
chloroethane	64	2.82	-	-
methylene chloride	84	4.03	3.8	5-10
trichlorofluoromethane	101	5.14	-	-
1,1-dichloroethylene	96	5.25	4.4	5-10
bromochloromethane (IS)	128	6.31	-	-
1,1-dichloroethane	63	6.48	7.4	5
trans-1,2-dichloroethylene	96	6.81	6.2	3
chloroform	83	7.70	8.3	1-2
1,2-dichloroethane	98	8.29	9.2	10(62)
1,1,1-trichloroethane	97	9.28	10.3	10
carbon tetrachloride	117	9.45	10.7	1-2
bromodichloromethane	127	10.36	12.4	5-10
bis-chloromethyl ether	79	10.50		
1,2-dichloropropane	112	11.30	13.1	10
trans-1,3-dichloropropene	75	11.70	-	-
trichloroethylene	130	11.98	13.9	5-10

(continued)

TABLE 19 (cont'd.)

Compound	Ion used to quantify	R.T., min (EPA)	R.T., min (RTI)	LOD, ng
dibromochloromethane	127	12.86	-	-
cis-1,3-dichloropropene	75	12.61	-	-
1,1,2-trichloroethane	97	12.61	15.2	3-5
benzene	78	12.95	13.5	0.2-0.5
2-chloroethylvinyl ether	106	13.71	-	-
2-bromo-1-chloropropane(IS)	77	13.82	-	-
bromoform	173	15.40	17.9	2-5
1,1,2,2-tetrachloroethylene	164	17.44	19.2	2
1,1,2,2-tetrachloroethane	168	17.70	19.8	<40
1,4-dichlorobutane(IS)	55	18.13	-	-
toluene	92	18.53	19.6	0.1-1
chlorobenzene	112	20.57	20.9	2
ethylbenzene	106	25.06	22.4	4
acrolein	56	no data		-
acrylonitrile	53	no data	5.00	25-50
o-dichlorobenzene	146	-	32.0	2
m-dichlorobenzene	146	-	34.0	5

TABLE 20. RELATIVE MOLAR RESPONSE FACTORS FOR SEVERAL PRIORITY POLLUTANTS USING SELECTED *M/Z* IONS

Priority pollutant	*m/z*	iS-PFB (*m/z*-186)	iS-PFT (*m/z*-236)
methyl bromide	94	0.104 ± 0.008[a]	0.076 ± 0.002
dichloromethane	84	0.139 ± 0.002	0.104 ± 0.007
1,1-dichloroethylene	96	0.341 ± 0.049	0.249 ± 0.041
acrylonitrile	53	0.037 ± 0.005	0.027 ± 0.003
1,2-*trans*-dichloroethylene	61	0.098 ± 0.016	0.070 ± 0.007
chloroform	83	0.093 ± 0.013	0.071 ± 0.016
1,2-dichloroethane	98	0.016 ± 0.005	0.011 ± 0.001
1,1,1-trichloroethane	97	0.119 ± 0.004	0.095 ± 0.013
carbon tetrachloride	117	0.075 ± 0.005	0.054 ± 0.004
bromodichloromethane	127	0.017 ± 0.004	0.013 ± 0.003
1,2-dichloropropane	112	0.004 ± 0	0.032 ± 0.004
benzene	78	0.024 ± 0.032	0.187 ± 0.038
trichloroethylene	130	0.071 ± 0.017	0.052 ± 0.013
bromoform	171	0.036 ± 0.007	0.026 ± 0.004
tetrachloroethylene	170	0.019 ± 0.003	0.013 ± 0.002
toluene	93	0.019 ± 0.002	0.014 ± 0.002
ethylbenzene	106	0.254 ± 0.047	0.184 ± 0.036
chlorobenzene	112	0.341 ± 0.048	0.248 ± 0.039
1,2-dichlorobenzene	150	0.039 ± 0.002	0.0295 ± 0
1,3-dichlorobenzene	150	0.015 ± 0.001	0.0115 ± 0

[a] Average of triplicate determinations.

SECTION 9

APPLICATION OF DEVELOPED METHODS TO THE COLLECTION AND ANALYSIS OF "PURGEABLE" PRIORITY POLLUTANTS EMITTED FROM MUNICIPAL TREATMENT FACILITIES

INTRODUCTION

The major objective of this program has been to develop, validate and apply a method to the collection and analysis of priority pollutants emitted from municipal treatment facilities. The procedure was to representatively sample air streams passing through wastewater in grit chambers and aeration basins and to analyze those representative samples for volatile toxic organics. The previous sections addressed the development and evaluation of individual facets of the collection and analysis systems. This section presents a further evaluation of the procedure and its application to different types of aeration systems including pure oxygen (closed chamber) activated sludge, conventional activated sludge, conventional grit chamber, and aerated grit chambers. One major aim was to determine the amounts of priority and other pollutants stripped from the water by an air flow in grit chambers and aeration basins in order to define the sampling volume _vs_. sample quantity for GC/MS/COMP analysis.

This section discusses the cumulative effort of the individual facets of the program previously described in Sections 5-8 and the application of the developed method to the collection and analysis of priority pollutants in air streams.

EXPERIMENTAL

Sampling of Open Aeration Basins

Integrated sampling of the air stream passing through wastewater at municipal treatment plants was accomplished using the prototype Nutech sampler (Nutech Corp., Durham, NC) described under Section 7. Flow rates were maintained at prescribed rates using the variable critical orifices. The flow through each of the three sampling cartridges and the total flow through all cartridges were monitored with a calibrated mass flow meter. The total flow from the aeration basin (minus the sampled volume) was registered on a dry gas meter; only a fraction (up to 30%) of the air stream to the sampling unit was sampled by the three Tenax GC cartridges.

Typically, sampling of aeration basins involved placing on the wastewater surface the gas sampling shroud which was supported by flotation collars and held in position by support arms fastened to the guard rails. The aeration rate passing through the wastewater was measured as a total gas flow into the gas meter plus the total volume sampled. The gas flow was expressed as ℓ/min/ft^2. Because the aeration rate can be highly variable across a basin, it was necessary to determine the aeration rate prior to sampling by simply passing the total flow of the drying gas meter for a short period of time (∿10 min).

Sampling volumes of 1, 3 and 5 ℓ/cartridge were used in these studies to determine the quantity of organic vapors that should be collected without overloading or saturating the instrumental analysis system. Triplicate cartridges were used in sampling.

Sampling was performed at the grit chamber and aeration basins at the South Burlington, NC and Durham, NC wastewater treatment plants. The sampling protocols are given in Table 21.

Sampling of Closed (Pure Oxygen) System

Continuous sampling for the priority pollutants in the vent from a closed chamber was accomplished using a Nutech Model 221-1A portable sampler (Nutech Corp., Durham, NC). The total flow was monitored through a calibrated flow meter to integrate the flow sample from all cartridges. The portable sampling unit was operated on a 12 v storage battery and was capable of continuous operation for a period of up to 24 hrs. Duplicate cartridges were deployed at the exhaust vent. The sampling head was connected to a vacuum line of ∿20 ft so that the sampler could be positioned at a distant location from the pure oxygen vent.

A 1-ℓ gas sample was taken over a period of 5 min.

Qualitative Analysis by Capillary GC/MS/COMP

Qualitative analysis was performed with a CH-7 GC/MS system equipped with a 620L computer. The organic vapors which were collected on the Tenax GC sampling cartridge were subjected to thermal desorption followed by capillary gas chromatography for the resolution of the complex mixture. An SE-30 stationary phase coated on a glass SCOT capillary (12,13) which was programmed from 25°C-240°C at 4°/min was used for effecting this resolution. The carrier flow (helium) was 2.5 ml/min. The operating parameters presented in Table 7 were used for the analysis of this sample.

Prior to running unknown samples, the system was calibrated by introducing a standard substance, perfluorokerosene, into the instrument and determining the time of appearance of the known standard peak in relation to the scanning field. Calibration curves which are thus generated were stored in computer memory. This calibration served only to calibrate the mass ion over the mass scanning range. The next stage of the data processing involved the mass conversion of the spectral peak times to peak masses which was done directly via the dual disk system. A mass conversion was accomplished by use of the calibration table obtained previously using perfluorokerosene (normally one set of the calibration data was sufficient

TABLE 21. SAMPLING PROTOCOL FOR MUNICIPAL TREATMENT FACILITIES

Municipal plant	Stream type	Location	Sampling cartridge			Total air stream vol. (ℓ)	Sampling rate (ml/min)			Sampling time (min.)	Date
			No. 1	No. 2	No. 3		No. 1	No. 3	No. 3		
South Burlington, NC	Raw Wastewater	Grit Chamber	1.02	1.09	1.01	33.58	291	311	289	3.5	8/1/78
	Activated Sludge	Aeration Basin/ Plug flow	1.00	1.05	1.03	32.90	285	300	294	3.5	8/1/78
Durham, NC	Activated Sludge	Aeration Basin/ Plug flow	1.00	1.00	1.00	28.76	103	102	105	10	7/21/78
Danville, VA	Activated Sludge	Pure Oxygen/ Closed Chamber	1.42	1.42	-	2.84	284	284	-	5	7/31/78

[a] Values are ℓ/cartridge.

for an entire day's data processing since the characteristics of the Hall probe were such that calibration variation was <0.2 amu/day).

The identity of the components in the sample was assigned on a grated scale. Positive identification was assigned for those compounds for which the observed spectrum matched library spectra and/or indices of tabulated spectra and the elution time and temperature corresponded with that of an authentic compound. For many cases where the isomeric forms could not be distinguished, the name of the compound as an isomer was indicated. In many cases only an empirical formula could be assigned since the mass cracking pattern of isomers were very similar (retention indices could not be available). In some cases a tentative identification was assigned when the mass cracking pattern yielded a similar match and no retention index was available for that compound.

Quantitative Analysis by GC/MS/COMP

The calibration of the GC/MS system for quantitative analysis of priority pollutants involved spiking Tenax GC sampling cartridges with known amounts of priority pollutants and internal standards perfluorobenzene and perfluorotoluene utilizing the previously described permeation system (10). Procedure for calibrating the GC/MS system and the determination of RMR's was also previously described (Section 8).

A Finnigan Model 3300 GC/MS system equipped with a PDP/12 computer was used. This system was described in Section 8.

RESULTS AND DISCUSSION

Figure 22 presents the GC/MS/COMP chromatographic profile of the volatile organics which were identified in air streams from an aeration basin at Durham, NC treatment plant. Approximately 100 discernable components were detected. Table 22 presents the volatile organics which were identified in the air stream. Several sulfur compounds and chlorinated hydrocarbons were identified. However, the majority of the components were hydrocarbons and alkyl-aromatics. Even using a 100-m glass SCOT column coated with SE-30, the resolution was inadequate to completely separate all the components, particularly those occurring between elution temperatures of 135°-195°C. Despite the complexity of the sample, many of the organics were identified. Furthermore, the use of the chromatographic conditions employing the packed column described earlier is effective in separating the volatile (purgeable) priority pollutants when used in combination with mass chromatography. The presence of many of the priority pollutants of interest which were identified in this sample confirms the previous methods-of-addition experiments since the previous data indicated the presence of priority pollutants which complicated the recovery studies.

Table 23 presents the analysis for priority pollutants in air streams from the grit chamber at South Burlington, NC. The sampling system described in Section 7 was used to sample the grit chamber (the sampling protocol was given in Table 21). The data indicate substantial concentrations

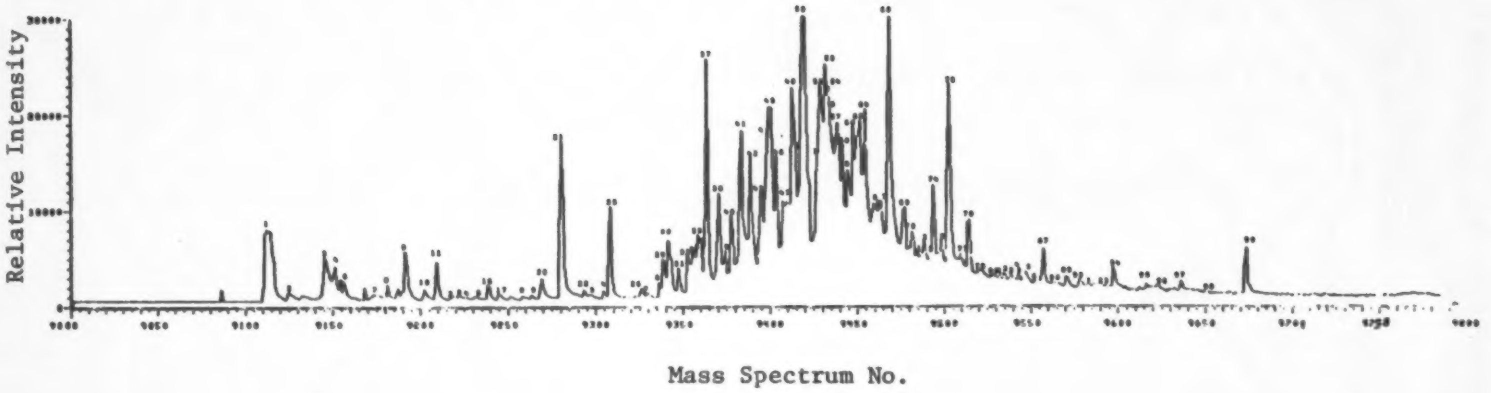


Figure 22. GC/MS/COMP chromatographic profile of volatile organics identified in air stream from aeration pond at Durham, NC Treatment Plant (see Table 22 for peak assignments).

TABLE 22. VOLATILE ORGANICS IDENTIFIED IN AIRSTREAM FROM AERATION BASIN (PLUG FLOW) AT DURHAM, NC PLANT[a]

Chromato-graphic peak no.	Elution temp. (°C)	Compound
1	58	CO_2
2	62	acetaldehyde + C_4H_8 isomer
2A	64	methyl ethyl ether (tent.)
3	69	acetone
4	71	diethyl ether
5	72	dimethyl sulphide
6	73	dichloromethane
6A	74	carbon disulphide
6B	78	C_4H_6O aldehyde isomer
7	79	1,1-dichloroethane
7A	79	vinyl acetate (tent.)
7B	80	methyl vinyl ketone
7C	81	methyl ethyl ketone
8	83	hexafluorobenzene (eS) + dichloroethylene isomer
8A	84	*n*-hexane
9	85	chloroform
9A	85	ethyl acetate
10	88	perfluorotoluene (eS)
10A	87	methylcyclopentane
10B	89	1,2-dichloroethane
11	91	1,1,1-trichloroethane
12	94	benzene
12A	94	carbon tetrachloride (traces) (tent.)
13	95	1-butanol
14	96	C_7H_{16} isomer
14A	97	$C_5H_{10}O$ aldehyde isomer
14B	98	3-methylhexane
15	98	*n*-pentanal
15A	100	$C_5H_{12}O$ isomer (tent.)
16	101	trichloroethylene
17	103	*n*-heptane
17A	103	2-thiapentane
18	107	ethyl isopropyl ether (tent.)
18A	108	C_7H_{14} isomer
19	109	dimethyl disulphide
20	111	acetic acid
21	115	toluene
22	119	*n*-hexanal
22A	119	C_8H_{16} isomer
23	120	C_8H_{16} isomer
23A	122	C_9H_{20} isomer
24	123	*n*-octane
25	124	tetrachloroethylene
26	130	trimethylcyclohexane
27	131	C_9H_{18} isomer
28	134	ethylbenzene
29	134	trimethylcyclohexane isomer
30	135	xylene isomer
30A	136	C_9H_{20} isomer
31	137	C_9H_{20} isomer
32	139	C_9H_{18} isomer
33	140	*o*-xylene
34	140	C_9H_{18} isomer
35	141	methylethylcyclohexane isomer
36	142	methylethylcyclohexane isomer
37	143	*n*-nonane + alkyl butyrate (tent.)
37A	143	$C_{10}H_{20}$ isomer
38	145	C_9H_{18} isomer
39	146	$C_{10}H_{22}$ isomer
40	147	C_9H_{16} + C_9H_{18} isomers
40A	148	$C_{10}H_{22}$ isomer
40B	148	$C_{10}H_{20}$ isomer
40C	149	C_9H_{18} isomer
41	149	$C_{10}H_{22}$ isomer
41A	151	benzaldehyde (traces)
42	151	$C_{10}H_{20}$ isomer + *n*-propylbenzene (traces)
42A	152	$C_{10}H_{18}$ isomer
42B	153	ethyltoluene isomer
43	153	$C_{10}H_{22}$ isomer
43A	154	$C_{10}H_{20}$ isomer
43B	154	1,3,5-trimethylbenzene
44	155	$C_{10}H_{22}$ isomer
45	155	$C_{10}H_{20}$ isomer
45A	156	$C_{10}H_{22}$ isomer
46	156	*o*-ethyltoluene
46A	157	$C_{10}H_{18}$ isomer
47	158	$C_{10}H_{20}$ isomer
47A	158	$C_{10}H_{20}$ isomer
48	159	1,2,4-trimethylbenzene + $C_{10}H_{20}$ isomer
49	160	$C_{10}H_{20}$ isomer
49A	161	dichlorobenzene isomer
49B	161	*n*-decane
50	162	dichlorobenzene + isomer
50A	162	C_4-alkyl benzene isomer
50B	163	$C_{11}H_{22}$ isomer
50C	164	C_4-alkyl benzene isomer

(continued)

TABLE 22 (cont'd.)

Chromato-graphic peak no.	Elution temp. (°C)	Compound
51	165	1,2,3-trimethylbenzene
51A	165	C_4-alkyl benzene isomer
52	165	$C_{11}H_{24}$ isomer
52A	166	$C_{11}H_{24}$ isomer
53	166	dichlorobenzene isomer
54	167	$C_{11}H_{24}$ isomer
55	167	$C_{10}H_{16}$ isomer
55A	167	$C_{10}H_{18}$ isomer
56	168	C_4-alkyl cyclohexane isomer
56A	168	$C_{11}H_{22}$ isomer
57	169	$C_{11}H_{24}$ isomer
57A	169	C_4-alkyl benzene isomer
58	170	C_4-alkyl benzene + $C_{11}H_{22}$ isomers
59	170	C_4-alkyl benzene isomer
59A	171	$C_{11}H_{22}$ isomer
59B	171	$C_{11}H_{24}$ isomer
60	172	$C_{11}H_{22}$ isomer
61	172	C_4-alkyl benzene + $C_{11}H_{24}$ isomers
62	173	$C_{10}H_{18}$ isomer
63	173	*n*-nonanal
64	174	$C_{11}H_{24}$ isomer
64A	174	C_4-âlkyl benzene isomer
64B	175	$C_{11}H_{22}$ isomer
65	175	C_4-alkyl benzene + C_4H_7-benzene isomers
65A	176	$C_{12}H_{22}$ isomer
66	176	$C_{11}H_{22}$ isomer
67	177	$C_{11}H_{22}$ isomer
67A	178	$C_{12}H_{24}$ isomer
68	178	*n*-undecane
68A	179	C_4-alkyl benzene isomer
68B	180	$C_{12}H_{26}$ isomer
68C	181	C_4-alkyl benzene isomer
69	181	$C_{12}H_{26}$ isomer
69A	182	$C_{11}H_{20}$ isomer
70	183	$C_{12}H_{26}$ isomer
70A	183	C_5-alkyl benzene isomer
71	184	$C_{12}H_{26}$ + alkyl phenol (tent.) isomers
71A	184	C_5-alkyl benzene isomer
72	185	$C_{11}H_{20}$ + $C_{12}H_{24}$ isomer
73	186	C_4H_7-benzene + $C_{12}H_{24}$ isomers
73A	186	C_4-alkyl benzene isomer
74A	187	C_5-alkyl benzene isomer
75	188	$C_{12}H_{26}$ isomer
76	190	$C_{10}H_{18}$ isomer
76A	190	trichlorobenzene isomer
76B	191	$C_{12}H_{22}$ isomer
77	192	$C_{12}H_{24}$ isomer
78	193	*n*-dodecane
78A	195	$C_{13}H_{26}$ isomer
78B	195	trichlorobenzene isomer (traces)
79	196	$C_{13}H_{28}$ isomer
80	198	unsat. hydrocarbon
81	200	$C_{13}H_{26}$ isomer
82	200	unsat. hydrocarbon
83	202	unsat. hydrocarbon
84	203	$C_{13}H_{26}$ isomer
85	205	$C_{13}H_{28}$ isomer
86	207	$C_{12}H_{24}$ isomer
86A	207	$C_{13}H_{28}$ isomer
87	208	*n*-tridecane
88	211	sat. hydrocarbon (tent.)
90	216	sat. hydrocarbon + C_3-alkyl phenol isomer (tent.)
91	217	$C_{14}H_{30}$ isomer
92	218	sat. hydrocarbon
93	219	$C_{14}H_{30}$ isomer
93A	221	$C_{14}H_{28}$ isomer
94	222	*n*-tetradecane
95	229	alkyl benzene + unsat. hydrocarbon
96	231	$C_{15}H_{32}$ isomer
97	235	sat. hydrocarbon

TABLE 23. ANALYSIS FOR PRIORITY POLLUTANTS IN AIR STREAM FROM GRIT CHAMBER AT SOUTH BURLINGTON, NC MUNICIPAL TREATMENT PLANT

Priority pollutants	ng/cartridge	ng/min/ft^2[a]	LOD[b] (ng/ℓ)
methyl bromide	ND	ND	5
dichloromethane	114 ± 7	1,140 ± 70	5-10
1,1-dichloroethylene	15 ± 2	15 ± 20	5-10
acrylonitrile	ND	ND	25-50
1,2-*trans*-dichloroethylene	188	1,880	3
chloroform	21,963 ± 8,316	219,630 ± 83,160	1-2
1,2-dichloroethane	548 ± 72	4,480 ± 720	10
1,1,1-trichloroethane	4,468 ± 668	44,680 ± 6,680	10
carbon tetrachloride	ND	ND	1-2
bromodichloromethane	260 ± 34	2,600 ± 340	5-10
1,2-dichloropropane	41,850 ± 4,950	418,500 ± 49,500	10
benzene	93 ± 5	930 ± 50	0.2-0.5
trichloroethylene	16,095 ± 1,705	160,950 ± 17,050	5-10
bromoform	ND	ND	2-5
tetrachloroethylene	54,000 ± 9,000	540,000 ± 90,000	2
1,1,2,2-tetrachloroethane	ND	ND	<40
toluene	31,835 ± 2,665	318,350 ± 26,650	0.1-1
ethylbenzene	3,275 ± 275	32,750 ± 2,750	4
chlorobenzene	38	380	2
1,2-dichlorobenzene	ND	ND	2
1,3-dichlorobenzene	88,500	885,000	5
1,1,2-trichloroethane	ND	ND	3-5

[a] 10 ℓ/min/ft^2

[b] LOD = limit of detection; calculated from LOD's in Table 19 and volume air sampled (1.0 ℓ).

(μg quantities) for a number of the priority pollutants that were present in the air stream. The reproducibility between the Tenax GC sampling cartridges was in most cases better than ±15%.

Table 24 presents the levels of priority pollutants in the air stream from the aeration basin at South Burlington, NC municipal waste treatment plant. Again many of the priority pollutants were detected; however, a comparison of this data with the results from the raw wastewater indicates a considerable decrease in the amount of priority pollutants even though the air-stream rate from the wastewater was ∿10 ℓ/min/ft^2 in both cases. The difference in concentrations between air streams from the raw wastewater and activated sludge suggests that a considerable quantity of the priority pollutants have been stripped by the air stream at the grit chamber (and by removal at other points in the process) prior to entering the aeration basin.

Table 25 presents additional data on the emission rates of priority pollutants from aeration of activated sludge at the Durham, NC treatment plant. Again, many of the priority pollutants were detected in the air stream at μg/min/ft^2 amounts. Supporting data are given in Appendix A.

Samples from the vent of a pure oxygen (closed chamber) system were taken at the Danville, VA municipal waste treatment plant. These results are shown in Table 26. Many of the priority pollutants which were detected in the samples taken at the South Burlington and Durham, NC plant were not detected in these samples.

The detection limits using the determined limits of detection from the thermal desorption GC/MS/COMP of authentic compounds in combination with sampling volumes employed at the various treatment plants are given in Tables 24-26. The combined sampling and analysis method provided low ng/ℓ sensitivities. Furthermore, a sampling volume of 1 ℓ was optimum in these cases (≥3 ℓ overloaded the analytical system).

Table 27 presents the recovery of priority pollutants from activated sludges which were purged using the designed sampler. In these experiments, 7 ℓ of water was placed into a rectangular glass tank, and the liquid was purged with clean air (up to 14 ℓ) and the entire air stream was directed through the designed sampler. In the first experiment, distilled water was placed in the glass tank and purged with air to determine the background from the system (Table 27). Subsequently, activated sludge from the Durham, NC plant was purged with air to determine the levels of priority pollutants present in the wastewater, and then the wastewater was spiked with increasing quantities of priority pollutants. Each time the wastewater was purged, and total flow directed to the Nutech sampler. At the end of the experiment, the glass tank was rinsed with distilled water and then filled and purged to determine the background that might have occurred as a "memory effect" in the transfer line between the sampling head and the sampler. The data in Table 27 indicate that no appreciable "memory effect" was observed when the umbilical transfer line was maintained at 40°C, even when sampling an air stream from the wastewater containing microgram quantities of priority pollutants (Table 27). This series of experiments indicated that the transfer line at 40°C minimizes the effect of adsorption

TABLE 24. ESTIMATION OF PRIORITY POLLUTANT LEVELS IN AIR STREAM FROM AERATION BASIN AT SOUTH BURLINGTON, NC MUNICIPAL WASTE TREATMENT PLANT

Priority pollutants	ng/cartridge	ng/min/ft^2[a]	LOD[b] (ng/ℓ)
methyl bromide	ND	ND	5
dichloromethane	117 ± 1	1,146 ± 9.8	5-10
1,1-dichloroethylene	ND	ND	5-10
acrylonitrile	ND	ND	25-50
1,2-*trans*-dichloroethylene	75 ± 7	735 ± 69	3
chloroform	3,472 ± 205	34,026 ± 2009	1-2
1,2-dichloroethane	320 ± 23	3,136 ± 225	10
1,1,1-trichloroethane	487 ± 35	4,773 ± 343	10
carbon tetrachloride	ND	ND	1-2
bromodichloromethane	52 ± 12	510 ± 118	5-10
1,2-dichloropropane	35,850 ± 2,350	351,330 ± 23,030	10
benzene	126 ± 24	1,235 ± 235	0.2-0.5
trichloroethylene	2,937 ± 277	28,728 ± 2,715	5-10
bromoform	ND	ND	2-5
tetrachloroethylene	19,300	189,140	2
1,1,2,2-tetrachloroethane	ND	ND	<40
toluene	570	5,586	0.1-1
ethylbenzene	262	2,568	4
chlorobenzene	190	1,862	2
1,2-dichlorobenzene	19	186	2
1,3-dichlorobenzene	2,700	26,460	5
1,1,2-trichloroethane	41,910	410,718	3-5

[a] 9.8 ℓ/min/ft^2

[b] LOD = limit of detection; calculated from LOD's in Table 19 and volume air sampled (1.0 ℓ).

TABLE 25. ESTIMATION OF PRIORITY POLLUTANT EMISSIONS RATE FROM AERATION OF ACTIVATED SLUDGE AT DURHAM, NC TREATMENT PLANT

Priority pollutants	ng/ℓ	ng/min/ft^2[a]	LOD[b] (ng/ℓ)
methyl bromide	ND	ND	5
dichloromethane	1,972 ± 85	5,048	5-10
1,1-dichloroethylene	ND	ND	5-10
acrylonitrile	126	322	25-50
1,2-*trans*-dichloroethylene	30 ± 38	756 ± 97	3
chloroform	11,980 ± 450	30,669 ± 1,152	1-2
1,2-dichloroethane	84 ± 22	215 ± 56	10
1,1,1-trichloroethane	6,741 ± 601	17,257 ± 1,539	10
carbon tetrachloride	108	276	1-2
bromodichloromethane	291 ± 22	744 ± 56	5-10
1,2-dichloropropane	ND	ND	10
benzene	2,519 ± 12	6,449 ± 325	0.2-0.5
trichloroethylene	4,934 ± 175	12,631 ± 448	5-10
bromoform	ND	ND	2-5
tetrachloroethylene	8,043 ± 354	20,590 ± 906	2
1,1,2,2-tetrachloroethane	ND	ND	<40
toluene	49,771 ± 4,416	127,413 ± 11,305	0.1-1
ethylbenzene	814 ± 86	2,083 ± 220	4
chlorobenzene	41 ± 4	104 ± 2	2
1,2-dichlorobenzene	3,451 ± 384	8,835 ± 983	2
1,3-dichlorobenzene	54,032 ± 7,152	138,321 ± 18,309	5
1,1,2-trichloroethane	ND	ND	3-5

[a] 2.56 ℓ/min/ft^2

[b] LOD = limit of detection; calculated from LOD's in Table 19 and volume air sampled/aeration rate.

TABLE 26. ESTIMATION OF PRIORITY POLLUTANT LEVELS IN VENT FROM PURE OXYGEN (CLOSED CHAMBER) SYSTEM AT DANVILLE, VA MUNICIPAL WASTE TREATMENT PLANT

Priority pollutant	ng/cartridge	ng/m^3	LOD[a] (ng/m^3)
methyl bromide	ND	ND	3,448
dichloromethane	331 ± 97	233,098 ± 68,309	3,448-6,896
1,1-dichloroethylene	ND	ND	3,448-6,896
acrylonitrile	ND	ND	17,241-34,000
1,2-*trans*-dichloroethylene	ND	ND	2,069
chloroform	490 ± 44	345,070 ± 30,985	690-1,379
1,2-dichloroethane	ND	ND	6,900
1,1,1-trichloroethane	26	18,309	6,900
carbon tetrachloride	ND	ND	690
bromodichloromethane	ND	ND	3,448-6,900
1,2-dichloropropane	ND	ND	6,900
benzene	ND	ND	137-344
trichloroethylene	138	97,183	3,448-6,900
bromoform	ND	ND	1,379-3,448
tetrachloroethylene	ND	ND	1,379
toluene	371	261,267	69-690
ethylbenzene	T	T	2,759
chlorobenzene	ND	ND	2,759
1,2-dichlorobenzene	ND	ND	1,379
1,3-dichlorobenzene	141 ± 16	99,296 ± 11,268	1,379
1,1,2-trichloroethane	940	66,971	2,069-3,448

[a] LOD = limit of detection; calculated from LOD's in Table 19 and volume of air sampled.

TABLE 27. RECOVERY OF PRIORITY POLLUTANTS FROM ACTIVATED SLUDGE (DURHAM, NC PLANT) USING DESIGNED SAMPLER[a]

Priority pollutants	Quantity added (ppb)				Distilled water[b]	
	0	1	10	100	Before	After
1,1-dichloroethylene	ND[b]	54 ± 2[c]	2,156 ± 663	6,591 ± 591	ND	ND
acrylonitrile	ND	68 ± 2	177 ± 30	1,458 ± 293	ND	ND
1,2-*trans*-dichloroethylene	ND	418 ± 66	4,482 ± 289	16,823 ± 4,501	ND	ND
chloroform	1,223	1,799 ± 39	12,149 ± 1,245	132,148 ± 15,013	650 ± 50	385 ± 6
1,2-dichloroethane	ND	168 ± 10	2,081 ± 460	15,880 ± 1,391	ND	ND
1,1,1-trichloroethane	51	461 ± 49	6,354 ± 580	24,516 ± 768	ND	ND
carbon tetrachloride	ND	329 ± 38	7,888 ± 550	38,554 ± 2,877	ND	ND
bromodichloromethane	ND	346 ± 17	3,869 ± 154	38,137 ± 6,307	ND	ND
1,2-dichloropropane	ND	503 ± 85	5,653 ± 555	32,182 ± 1,182	ND	ND
benzene	270	657 ± 64	2,395 ± 55	59,652 ± 6,328	71 ± 1	ND
trichloroethylene	331	1,029 ± 193	11,618 ± 220	35,550 ± 2,832	ND	54
bromoform	ND	158	4,371 ± 143	51,092 ± 17,792	ND	ND
tetrachloroethylene	ND	163 ± 95	4,327 ± 380	26,095 ± 5,925	ND	ND
toluene	ND	2,212 ± 416	13,497 ± 383	65,611 ± 2,250	1,742 ± 2	1,543 ± 185
ethylbenzene	43	217 ± 12	1,886 ± 8	5,433 ± 406	12 ± 1	14 ± 4
chlorobenzene	ND	195 ± 24	2,911 ± 176	16,325 ± 1,070	65 ± 1	120 ± 15
o-dichlorobenzene	ND	162 ± 12	2,492 ± 146	24,892 ± 2,743	ND	67 ± 3
m-dichlorobenzene	ND	2,471 ± 336	11,175 ± 475	116,003 ± 14,685	150 ± 5	535 ± 17

[a] ND = not detected.

[b] Values are in ng and an average of triplicate determinations.

[c] 7 ℓ of activated sludge mixed liquor was placed in a retangular glass tank, purged with clean air and the air stream sampled with designed sampler.

[d] Distilled water was purged before and after experiments to determine memory affects from umbilical line.

of priority pollutants when sampling at high concentrations. The potential for contamination of subsequent samples appeared to be extremely low.

CHAPTER 10

ACCURACY AND PRECISION OF "PURGEABLE" PRIORITY POLLUTANT COLLECTION AND STORAGE

INTRODUCTION

This section describes the quantitative capability of the developed sampling and analysis technique. The objectives were to examine the recovery of purgeable radiotracer organics from organic-free water, raw wastewater and activated sludge from a laboratory vessel. The distribution of the radioactive pollutant between the liquid and gas phases was examined, as well as the recoveries of organics from the gas phase by the Tenax GC sampling cartridge.

Further studies were also conducted on the accuracy of sampling, utilizing the Nutech Model 851 sludge sampler, by examining the collection and recovery of radiotracer "purgeable" priority pollutants added to the airstream from activated sludge. This study served to determine the accuracy of collection of priority pollutants during stripping of the municipal and activated sludge waters.

Also, an assessment was made of the recovery of priority pollutants from the Tenax GC sampling cartridge after a period of storage. The use of radiotracer priority pollutants allowed the determination of mass balances in the experiments.

EXPERIMENTAL

Recovery of Radiotracer Priority Pollutants From Aqueous Matrices

A series of radiotracer priority pollutants which were commercially available were used for confirmation of recovery from aqueous matrices. These are listed in Table 28. Priority pollutants were selected to cover a range of volatility and solubility in water.

Experiments were performed by adding individual isotopes to: (1) organic-free water; (2) raw wastewater, and (3) activated sludge in a laboratory vessel (Fig. 23). The aqueous matrix was purged using two parts of air to one part of liquid (v/v). Listed in Table 28 are the quantities of isotopes used and the disintegrations/minute (dpm). The radiotracer compound was purged from the aqueous matrices and collected on a Tenax GC sampling cartridge which was previously described in Section 5. The recovery experiments were conducted in quintuplicate. The apparatus shown in Figure 24 was used to investigate the ^{14}C-labeled compound recovered from

TABLE 28. QUANTITY OF RADIOLABELLED PRIORITY POLLUTANTS USED IN RECOVERY EXPERIMENTS

Chemical	Quantity of isotope added µg (dpm)
Chloroform-^{14}C	23.0 (13.75×10^5)
Carbon Tetrachloride-^{14}C	6.0 (3.00×10^5)
Benzene-^{14}C	10.8 (32.50×10^5)
Toluene-^{14}C	12.0 (5.50×10^5)
Chlorobenzene-^{14}C	2.9 (5.25×10^5)
Bromobenzene-^{14}C	5.0 (15.25×10^5)

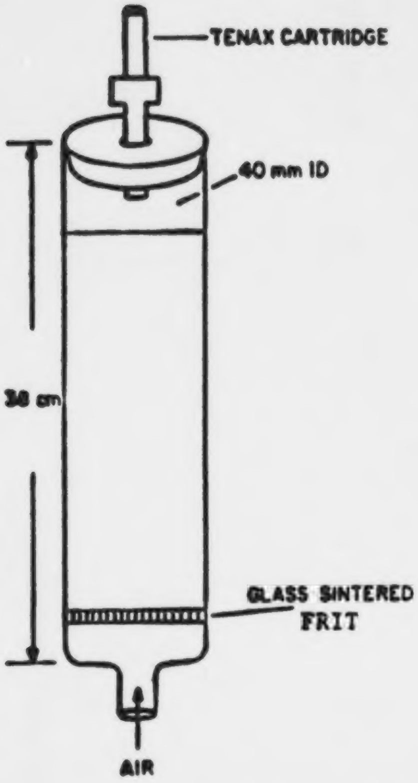

TENAX CARTRIDGE
40 mm ID
38 cm
GLASS SINTERED FRIT
AIR

Figure 23. Vessel employed in radiolabeled priority pollutant studies.

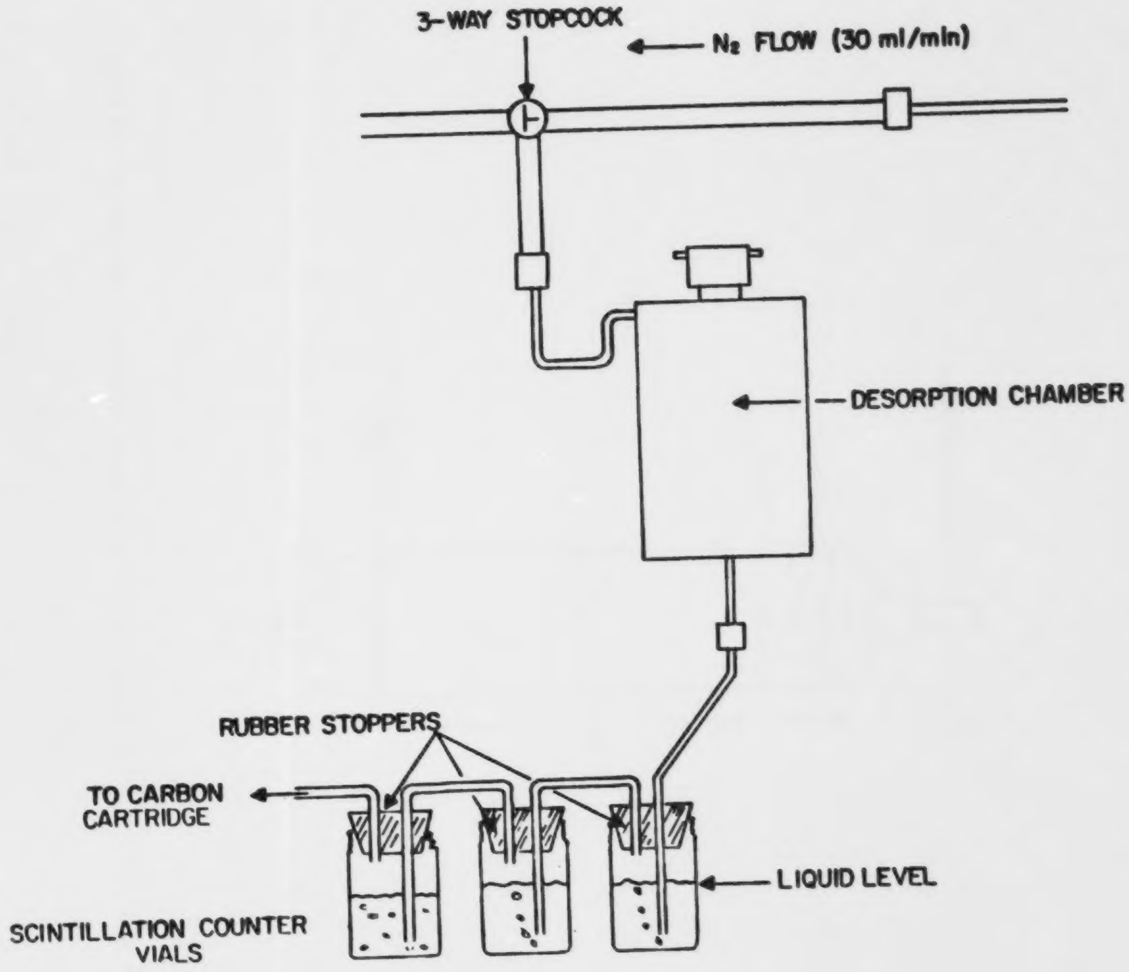

3-WAY STOPCOCK
N₂ FLOW (30 ml/min)
DESORPTION CHAMBER
RUBBER STOPPERS
TO CARBON CARTRIDGE
LIQUID LEVEL
SCINTILLATION COUNTER VIALS

Figure 24. Desorption apparatus for radioisotopically labelled compounds on Tenax GC.

the spiked matrices. Solutions of the ^{14}C-labeled compound were dissolved in methanol and added at levels of 5-40 ppb ($\sim$3-15 x 10^5 dpm). The total carrier volume (methanol) was 250 µl.

Table 29 presents the purging condition employed in this experiment. After purge and trap was completed, the Tenax GC sampling cartridges were thermally desorbed in the chamber (Fig. 24) for 10 min at 270°C with a purge rate of 30 ml/min. The effluent gas was bubbled through 15 ml of Triton-X scintillation counting fluid (cocktail) and 3 tandem scintillation vials (Fig. 24). Each scintillation vial of the triplicate series was individually counted on a Packard Tricarb 3375 liquid scintillation spectrometer to determine the total radioactivity recovered by thermal desorption of the Tenax GC cartridge. Also breakthrough of radioactivity was determined between the first, second or third tandemly arranged scintillation vials (Fig. 24). The radiotracer sample was counted until a standard error of 2.5 was obtained. The scintillation fluid was 6.0 g Omnifluor (New England Nuclear, Boston, MA) per liter of toluene. Observed radioactivity was corrected for quenching by the external standard ratio method and all counts were converted to dpm.

Standards for each radiotracer priority pollutant were prepared in quintuplicate by injecting with a Lambda® pipette (250 µl; this pipette was used for loading all aqueous matrices) directly into the counting vial containing 15 ml of Triton-X cocktail. The percent of compound recovery was calculated as follows: recovered = (dpm found in first + second + third scintillation vial) ÷ (average dpm found in the standard x (100). The trapping efficiency for 15 ml of Triton-X cocktail in the first vial was determined, as well as for the second vial, to ensure that breakthrough had not occurred. The possibility of breakthrough of compounds from the Tenax GC cartridge during the purge and trap of the ^{14}C-labeled spiked aqueous matrix was also investigated by using a second cartridge which was placed in tandem behind the first Tenax cartridge. Each was individually thermally desorbed into three fresh vials of Triton-X cocktail. Thus, the amount of radioactivity appearing on the second backup cartridge was determined. No radioactivity appeared in the backup Tenax GC cartridge for any of the priority pollutants studied.

Accuracy of Sampling

The accuracy and reproducibility of trapping priority pollutants from an air stream leaving activated sludge and municipal wastewater onto Tenax GC sampling cartridge was studied. The efficiency of transfer of priority pollutants through the transfer line of the model 851 sampler was determined, and the potential memory effects which might occur within the transfer line between sampling periods was assessed.

The sampler under evaluation was shown in Figure 18. A schematic diagram of the pneumatic was also shown in Figure 25. Triplicate Tenax GC sampling cartridges with backup cartridges were used to determine accuracy and precision. Six liters of activated sludge from the Northside Treatment Facility in Durham, NC was placed in a 9 ℓ glass vessel and purged using the parameters described in Table 30. Upon initiating the purging of activated

TABLE 29. PARAMETERS USED FOR RECOVERY EFFICIENCY STUDIES OF PRIORITY POLLUTANTS, SIMULATING MUNICIPAL TREATMENT FACILITY OPERATIONS

Parameter	Set point
Liquid Volume Purged	400 ml
Air Volume Purged	800 ml
Purge Rate	100 ml/min
Time	8 min
Volume of Isotope + Carried Added	250 μℓ

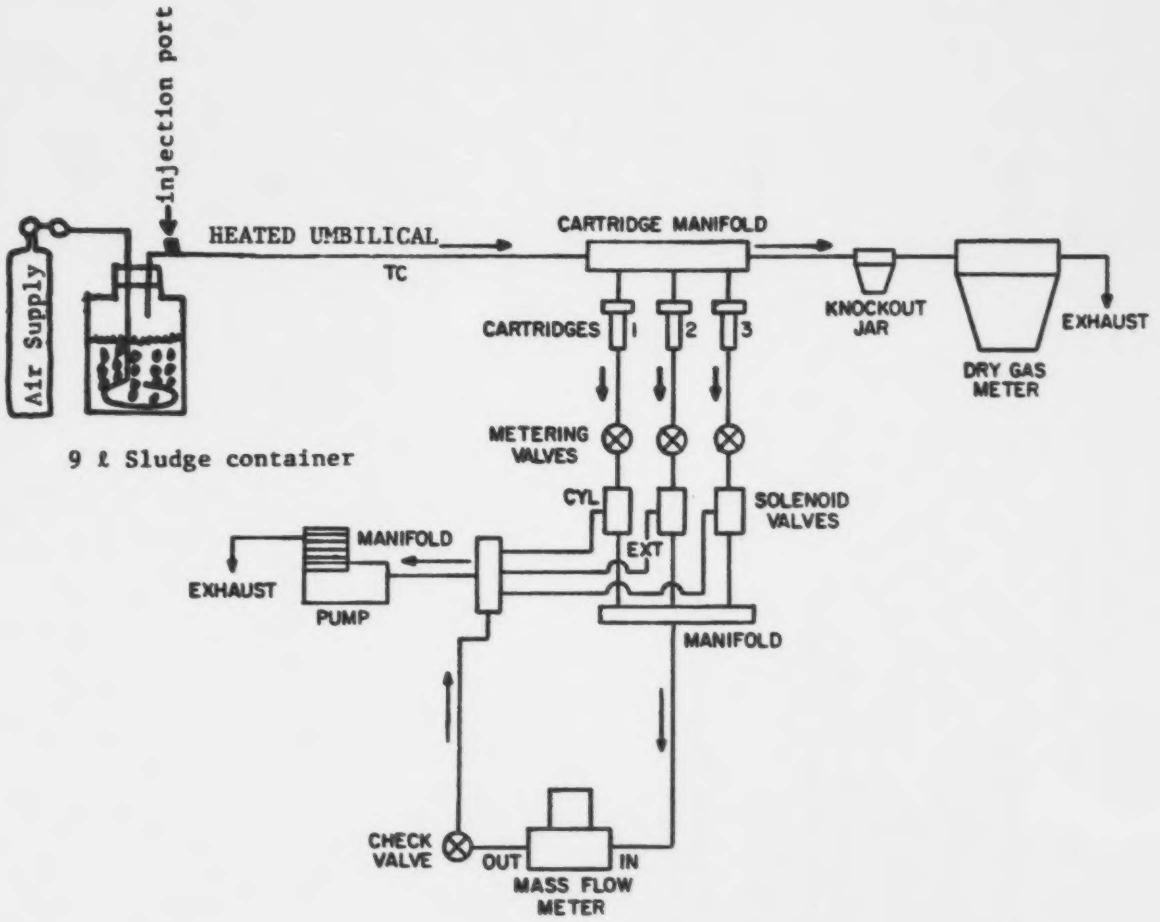

injection port
Air Supply
HEATED UMBILICAL
TC
9 ℓ Sludge container
CARTRIDGE MANIFOLD
CARTRIDGES
1
2
3
KNOCKOUT JAR
DRY GAS METER
EXHAUST
METERING VALVES
CYL
EXT
SOLENOID VALVES
MANIFOLD
MANIFOLD
EXHAUST
PUMP
MANIFOLD
CHECK VALVE
OUT
IN
MASS FLOW METER

Figure 25. Diagram of pneumatics in sampler system.

TABLE 30. PARAMETERS USED FOR DETERMINING SAMPLING PRECISION, ACCURACY, AND "MEMORY EFFECT"

Parameters	Condition
Volume activated sludge purged	6 ℓ
Purge rate	1.2 ℓpm
Purge volume	12 ℓ
Transfer line temperature	40°C
Sampling rate/cartridge (performed in triplicate)	300 mℓ/min
Sampling time	10 min
No. of tandem Tenax cartridges	2

sludge at a rate of 1.2 ℓ/minute, the radiotracer priority pollutant was injected into the heated umbilical transfer line (Table 31) and sampling was conducted at a rate of 300 ml/minute/cartridge. Sampling was continued for 10 min. After sampling was completed, the cartridges were replaced with an unexposed set and the transfer line was further purged for 10 additional minutes with a clean air supply, prior to the next collect to be performed. In each case when the experiment was repeated, fresh activated sludge from the aeration pond was also placed in the glass purging vessel. Experiments were performed in duplicate to determine accuracy and precision for each priority pollutant.

Radiotracer priority pollutants were recovered by thermally desorbing the radiolabeled compound from the Tenax GC sampling cartridge into the Triton-X scintillation cocktail (Fig. 24). Determination of dpm was continued until a standard error of 2.5% was achieved for each radioactive sample. The sampling accuracy was calculated by ratioing the observed radioactivity on the front and backup Tenax cartridges to the amount of radioactive priority pollutant injected into the umbilical transfer line. The fraction of the total sample which was collected by each Tenax GC cartridge was taken into account for each of the three replicates. Reproducibility of sampling was calculated as an average for the three front cartridges and three backup cartridges.

An investigation was conducted of the potential "memory effects" of priority pollutants occurring in the heated transfer line as a result of sampling airstreams spiked with radiotracer priority pollutants. After completing the sampling the transfer line was purged with 12 ℓ of clean air and the radioactivity in the line was determined by sampling the air passing through the transfer line with fresh Tenax GC cartridges (subsequent to each of the experiments for determining sampling precision and accuracy).

Sample Storage Study

The recovery of priority pollutant (from stored Tenax samples) from the airstream passing from the activated sludge aeration basin was performed using a Nutech 851 sampler. A total of 16 replicate cartridges were collected with five blanks serving as controls. The priority pollutants present in the aeration gases were determined by GC/MS/COMP techniques as described in Section 8 and for those priority pollutants which were detected, each one was quantified at intervals over a three-week period. Initially, the day after sampling was completed, the priority pollutant concentration was determined and then again at 1, 2 and 3-week intervals. Each analysis was conducted in triplicate. Samples were stored at -20°C.

RESULTS AND DISCUSSION

Recovery of Radiotracer Priority Pollutants From Aqueous Matrices

Table 32 presents the recovery of the radiotracer priority pollutants from distilled water (organic free), raw wastewater and activated sludge from the Northside Treatment Facility in Durham, NC. The values are given as the average percent of five determinations with corresponding standard deviation.

TABLE 31. LEVELS OF PRIORITY POLLUTANTS ADDED TO AIR STREAM FROM ACTIVATED SLUDGE[a]

Priority pollutant	Quantity used (ng)
Methyl bromide	1,050
Chloroform	460
Carbon tetrachloride	60
Benzene	215
Toluene	240
Chlorobenzene	57
Bromobenzene	100

[a] 12 ℓ of air was purged through 6 ℓ of activated sludge.

TABLE 32. RECOVERY OF RADIOISOTOPICALLY LABELLED PRIORITY POLLUTANTS FROM DISTILLED WATER, RAW WASTEWATER, AND SLUDGE

Chemical	Percent recovery		
	Distilled water	Raw wastewater	Activated sludge
Chloroform	26 ± 1 (1.4)[a]	30 ± 1 (4.5)	39 ± 7 (41)
Carbon tetrachloride	86 ± 2 (3.1)	58 ± 4 (6.9)	68 ± 1 (3.3)
Benzene	37 ± 3 (10)	40 ± 3 (12)	42 ± 2 (5.4)
Toluene	54 ± 3 (10)	49 ± 4 (18)	45 ± 2 (7.5)
Chlorobenzene	30 ± 1 (8.4)	32 ± 1 (8.2)	26 ± 1 (6.4)
Bromobenzene	24 ± 2 (17)	22 ± 1 (9.8)	26 ± 1 (12)

[a] Values are average percentages of five determinations with ± S.D.; coefficient of variation is in parentheses (S.D. ÷ Mean x 100).

The coefficient of variation is in parenthesis. For the six radioisotopically labeled priority pollutants virtually little variation was observed among organic-free water, raw wastewater and activated sludge. However, these recoveries are somewhat lower than those obtained with the purge-and-trap vessels employed for priority pollutant analysis. This is expected since the ratio between the volume of gas purged through the aqueous matrix and the volume of aqueous matrix is considerably lower than that employed in the standard purge-and-trap devices.

Sampling Precision and Accuracy

Table 33 presents the sampling precision for selected priority pollutants using Tenax GC sampling cartridges. For all priority pollutants studied, the sampling precision for the compounds was at least within ±10%. The collection efficiency was essentially quantitative for the first Tenax cartridge in the sampling train as determined by the amount of priority pollutants distributed between the front and backup Tenax cartridge.

Table 34 presents the sampling accuracy for a few priority pollutants using these sampling devices. For the compounds studied, quantitative recoveries were observed except for bromobenzene, which because of its lower vapor pressure was partially trapped on the aerosol filter.

The memory effect contribution in the sampler transfer line from sampling airstream containing priority pollutants was also examined. After completing the collection of each priority pollutant to determine the sampling accuracy and precision, the transfer line was further purged with clean air for a total of 10 min (12 ℓ), and then the background of the transfer line was determined. These results are given in Table 35. Indicated are the total radioactivity (dpm) sampled in the previous experiments and the dpm observed after purging of the sampler transfer line. In all cases, the percent memory effect was <0.2%.

The data presented in Tables 33-35 indicate that the Tenax sampling cartridge provides quantitative collection of priority pollutants in airstreams leaving grit chambers and activated sludge aeration basins. Furthermore, cross contamination of samples from one sampling period to the next is essentially negligible with this sampling system.

Sample Storage Study

A study was performed to determine the recovery of priority pollutants from stored Tenax samples collected from the airstream of an activated sludge aeration basin. The results of the recovery study are given in Table 36. The data represent the means and standard deviations for triplicate analyses with values in ng/3 ℓ of sample volume. Also included is the subsequent percent recovery (given in parenthesis) which was taken as 100% for the initial determination (day 1).

The recovery of chloroform decreased from 100% to 50% after three weeks of storage. For the remaining priority pollutants which were detected in these samples, the recovery was essentially quantitative after three weeks of

TABLE 33. SAMPLING PRECISION AND COLLECTION EFFICIENCY FOR SELECTED PRIORITY POLLUTANTS USING TENAX GC SAMPLING CARTRIDGES

Priority pollutant	Expt. No. 1[a]		Expt. No. 2	
	Front	Back	Front	Back
Methyl bromide	62 ± 6	37 ± 4	-	-
Chloroform	93 ± 2	7 ± 3	98 ± 3	7 ± 4
Carbon tetrachloride	77 ± 13	23 ± 10	92 ± 1	18 ± 1
Benzene	95 ± 3	5 ± 4	98 ± 0	2 ± 0
Toluene	93 ± 2	7 ± 2	94 ± 2	6 ± 2
Chlorobenzene	86 ± 1	14 ± 1	83 ± 17	15 ± 15
Bromobenzene	80 ± 6	20 ± 9	75 ± 2	25 ± 3

[a] Each experiment was conducted using triplicate cartridge sets (front and back cartridges); values are in percent with ± S.D.

TABLE 34. SAMPLING ACCURACY FOR SELECTED PRIORITY POLLUTANTS USING TENAX GC SAMPLING CARTRIDGES

Priority pollutant	Expt. no. 1[a]	Expt. no. 2
Chloroform	119 ± 27	106 ± 25
Carbon tetrachloride	78 ± 22	80 ± 5
Benzene	87 ± 25	94 ± 3
Chlorobenzene	96 ± 10	104 ± 14
Bromobenzene	50 ± 22	55 ± 10

[a] Each experiment was conducted in triplicate, values are in percent of [illegible] value with ± S.D.

TABLE 35. "MEMORY EFFECT" CONTRIBUTION IN SAMPLER TRANSFER LINE FROM SAMPLING AIR STREAMS CONTAINING PRIORITY POLLUTANTS

Priority pollutant	Total dpm[a] sampled (ng)	Residual dpm observed	Percent "memory"
Methyl bromide	1.5×10^5 (1,050)	144	0.08
Chloroform	5.5×10^5 (460)	166	0.03
Carbon tetrachloride	1.2×10^5 (60)	276	0.23
Benzene	1.3×10^5 (215)	130	0.01
Toluene	2.2×10^4 (240)	45	0.20
Chlorobenzene	2.1×10^4 (57)	29	0.14
Bromobenzene	6.1×10^4 (100)	114	0.19

[a] Represents total radioactivity and mass of priority pollutant sampled through line, followed by a 12-liter purge with clean air and then checked for residual radioactivity in transfer line.

TABLE 36. RECOVERY OF PRIORITY POLLUTANTS FROM STORED TENAX SAMPLES[a]

	Storage Time			
Chemical	1 da	1 wk	2 wk	3 wk
Chloroform	1,366 ± 186 (100)	1,137 ± 187 (83 ± 14)	667 ± 54 (49 ± 4)	655 ± 65 (48 ± 5)
1,1,1-Trichloroethane	3,884 ± 213 (100)	3,868 ± 888 (99 ± 22)	3,210 ± 625 (83 ± 16)	2,869 ± 383 (74 ± 10)
Trichloroethylene	1,651 ± 163 (100)	1,443 ± 286 (87 ± 17)	1,179 ± 119 (71 ± 7)	1,166 ± 8 (71 ± 1)
Benzene	141 ± 12 (100)	151 ± 37 (107 ± 26)	97 ± 11 (69 ± 8)	91 ± 2 (64 ± 1)
Tetrachloroethylene	6,424 ± 395 (100)	5,887 ± 631 (92 ± 1)	4,992 ± 289 (78 ± 4)	4,535 ± 96 (71 ± 1)
Toluene	2,368 ± 88 (100)	2,361 ± 306 (99 ± 13)	1,714 ± 54 (72 ± 2)	1,839 ± 113 (78 ± 5)
Ethylbenzene	261 ± 17 (100)	250 ± 39 (96 ± 15)	229 ± 1 (88 ± 1)	216 ± 4 (83 ± 1)
o-Dichlorobenzene	1,364 ± 92 (100)	1,221 ± 207 (89 ± 15)	1,162 ± 45 (85 ± 3)	1,082 ± 38 (79 ± 3)
Chlorobenzene[b]	T	T	10 ± 1	T
Bromodichloromethane[c]	T	T	55 ± 5	T
Dichloromethane	ND	ND	ND	ND

(continued)

TABLE 36 (cont'd.)

Chemical	Storage Time			
	1 da	1 wk	2 wk	3 wk
1,1-Dichloroethane	ND	ND	ND	ND
Carbon tetrachloride	T	T	T	T

[a] Values are ng/3 ℓ sample volume, percent recovered is given in parenthesis.

[b] Limit of detection ≈ 5 ng.

[c] Limit of detection ≈ 50 ng.

storage at -20°C. As the volatility of the priority pollutants decreased, the corresponding recovery improved (the standard deviation also decreased). For priority pollutants which were detected at trace levels immediately after sampling, they were also detectable in trace quantities after three weeks storage.

During the GC/MS/COMP analysis, a search was made for all of the priority pollutants which might be considered as "purgeable" in these samples. However only those given in Table 36 were found.

The accuracy and precision of collecting, storing and analysis of purgeable priority pollutants are satisfactory for the purpose of designating this procedure as a quantitative method.

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15. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants", U. S. E. P. A., Cincinnati, OH, April 1977. 134 pp.

APPENDIX A

VOLATILE ORGANICS IN AIR STREAM FROM GRIT CHAMBER

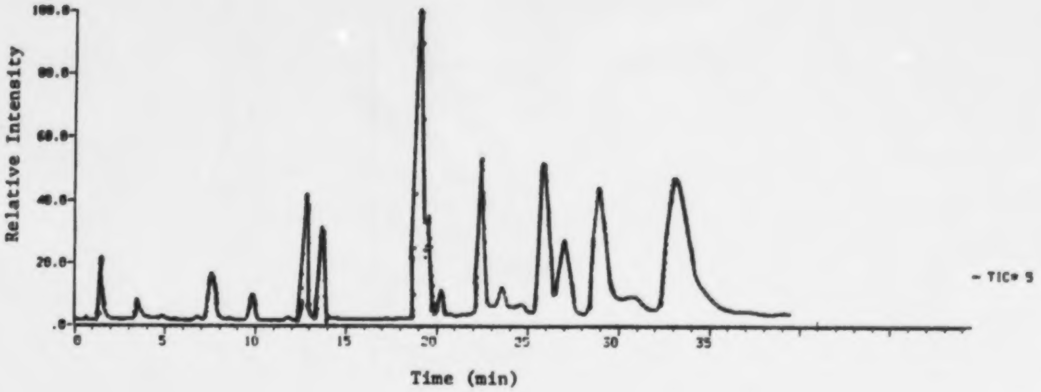


Figure A1. Reconstructed GC/MS chromatogram of volatile organics in air stream from grit chamber at S. Burlington, NC Treatment plant (Sample 1, 1.0 ℓ).

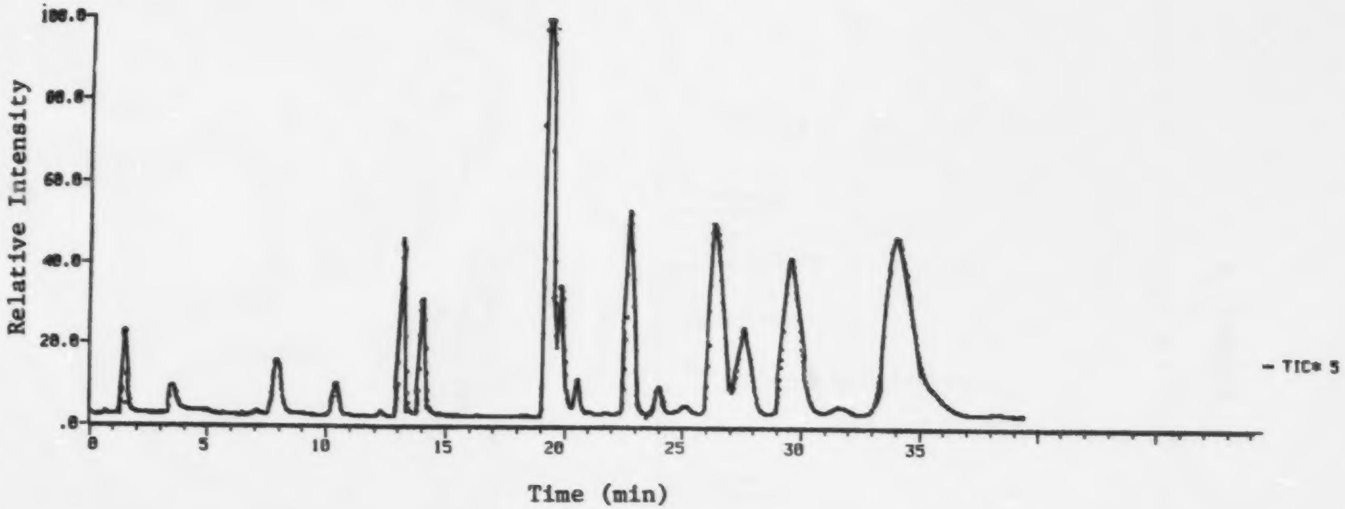


Figure A2. Reconstructed GC/MS chromatogram of volatile organics in air stream from grit chamber at S. Burlington, NC Treatment Plant (Sample 2, 1.0 ℓ).

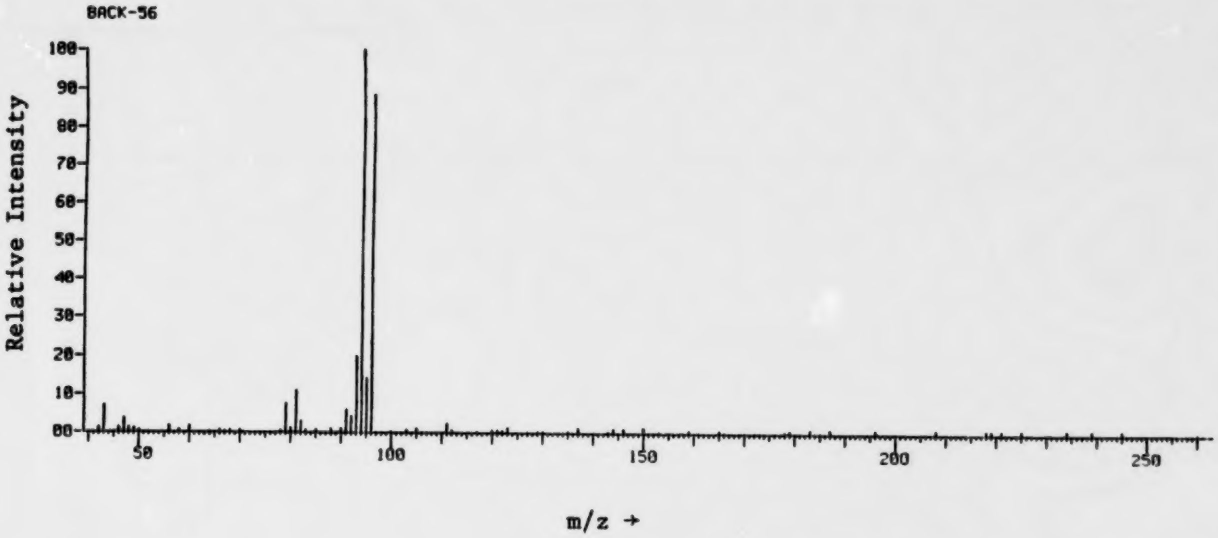


Figure A3. Mass spectrum of peak at 2.0 min.

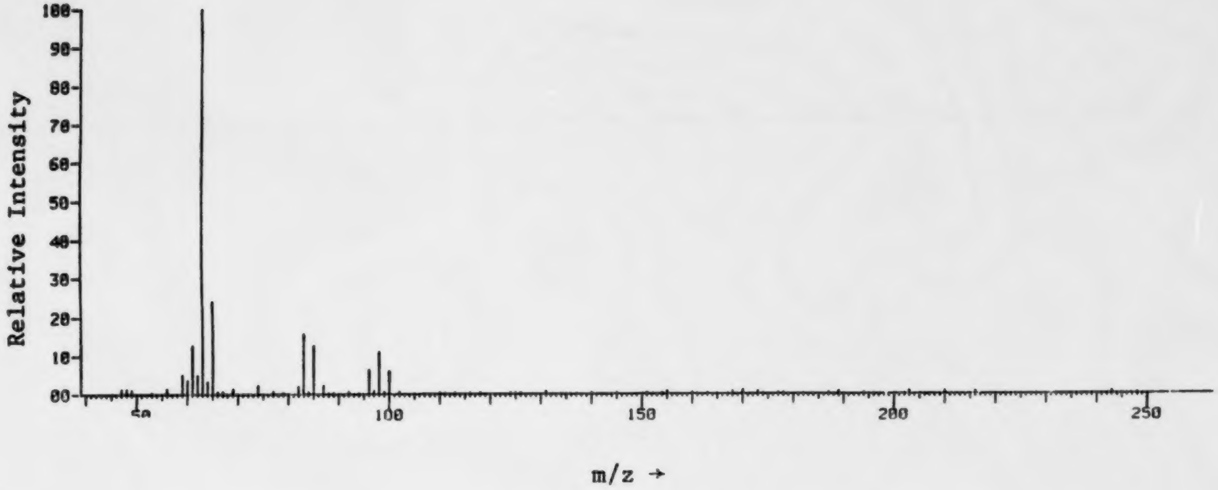


Figure A4. Mass spectrum of peak at 6.06 min.

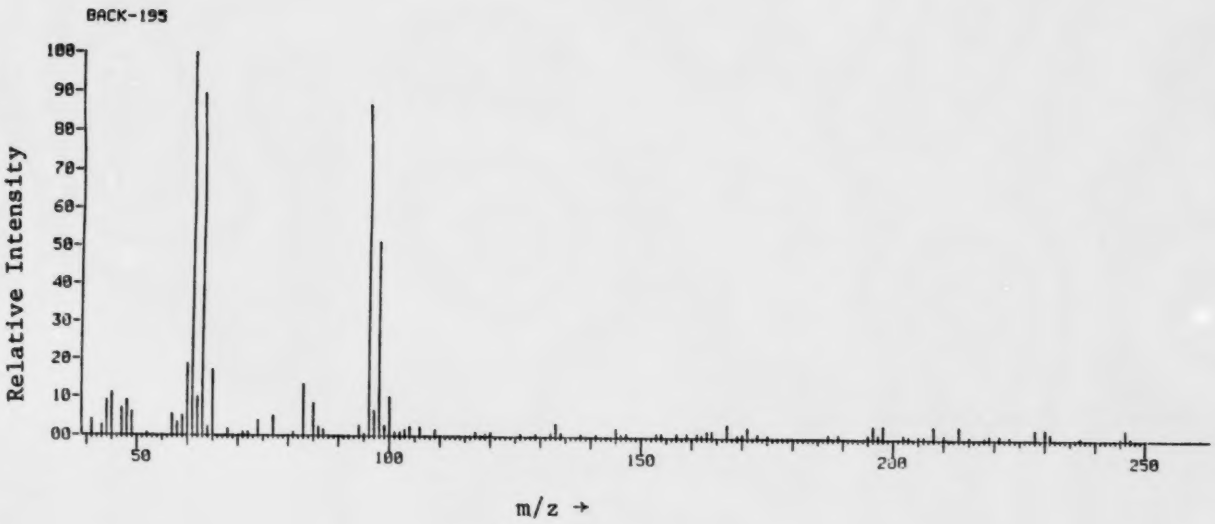


Figure A5. Mass spectrum of peak at 6.26 min.

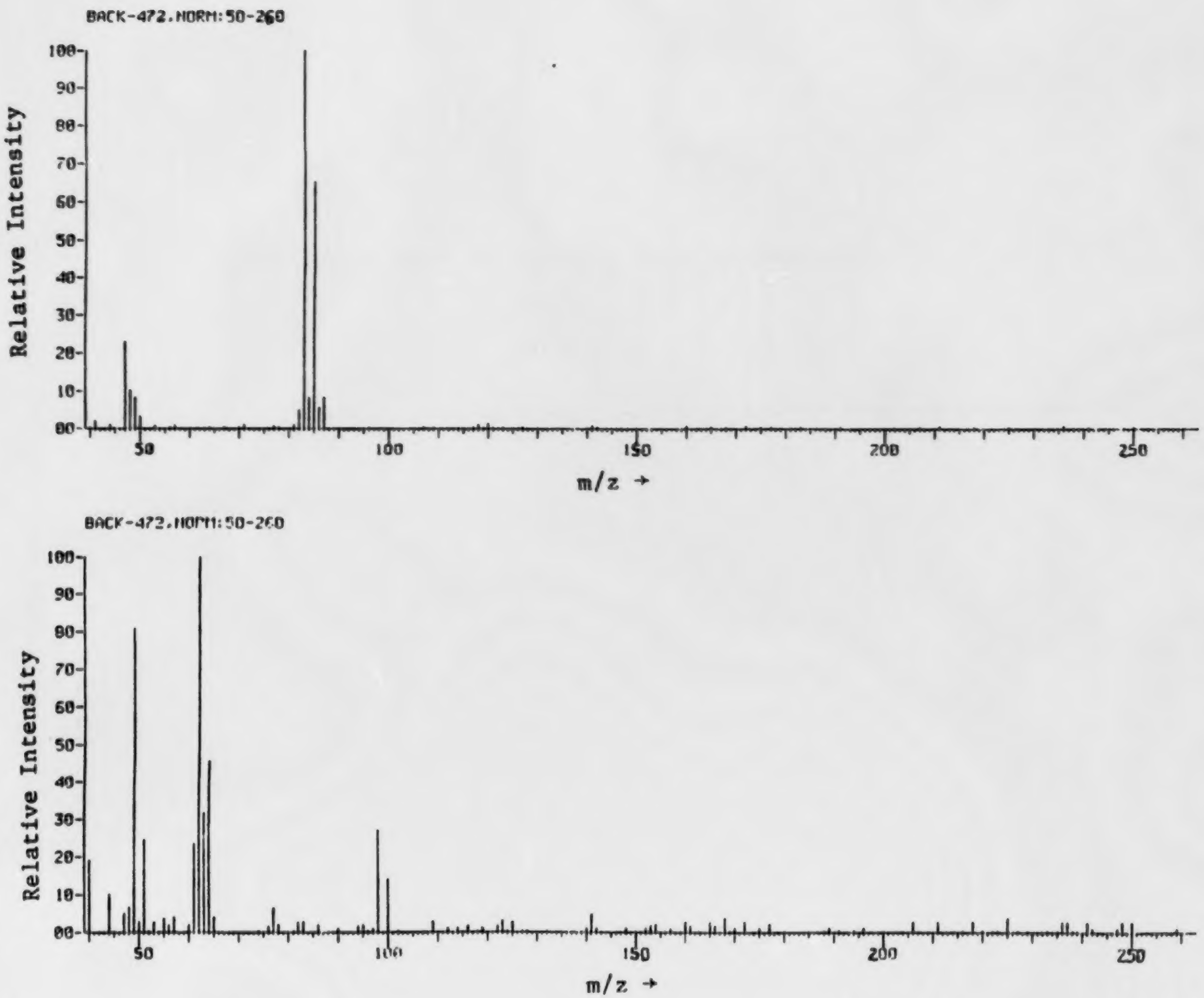


Figure A6. Mass spectra of peaks at 8.49 and 9.29 mins.

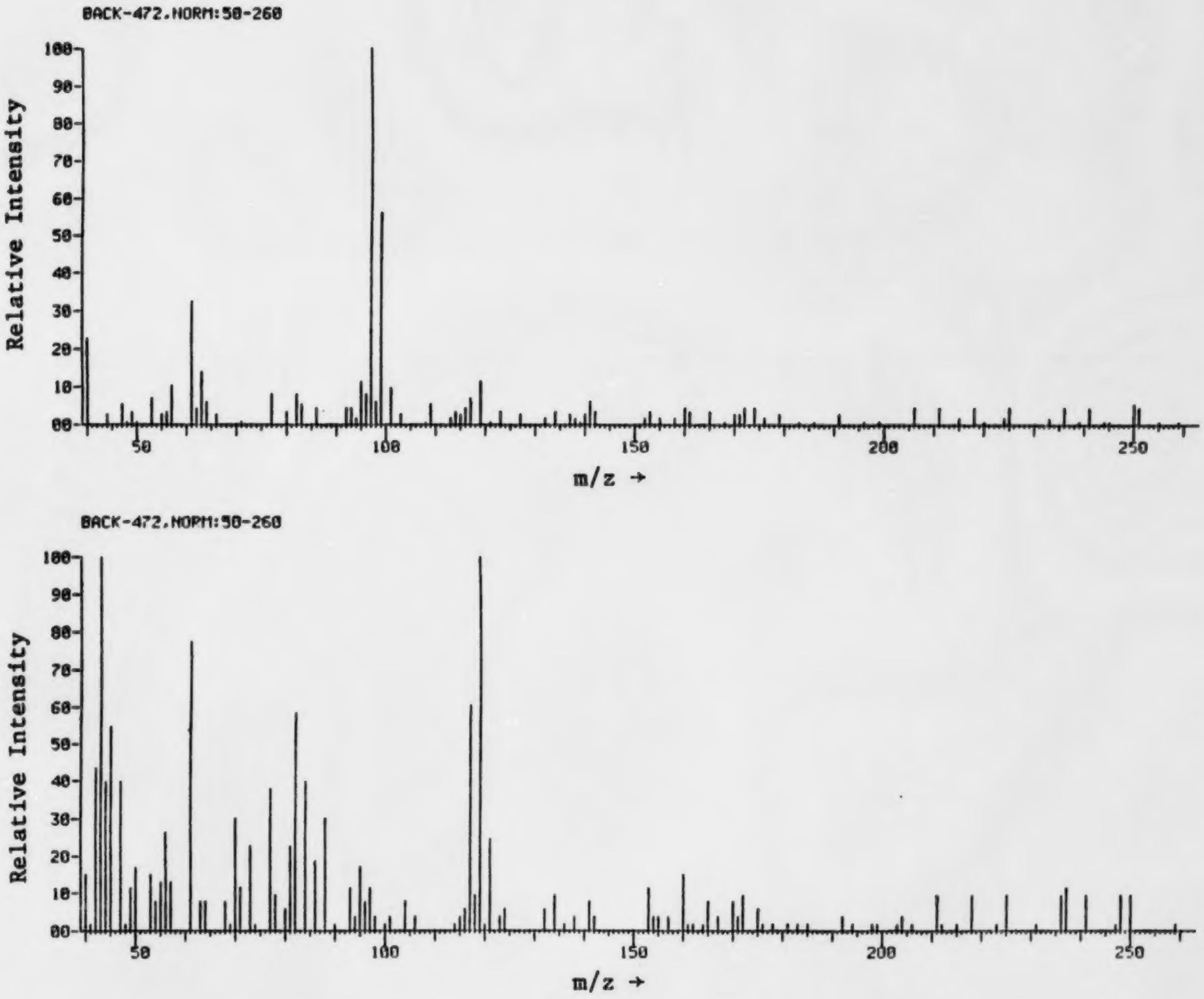


Figure A7. Mass spectra of peaks 10.33 and 10.86 min.

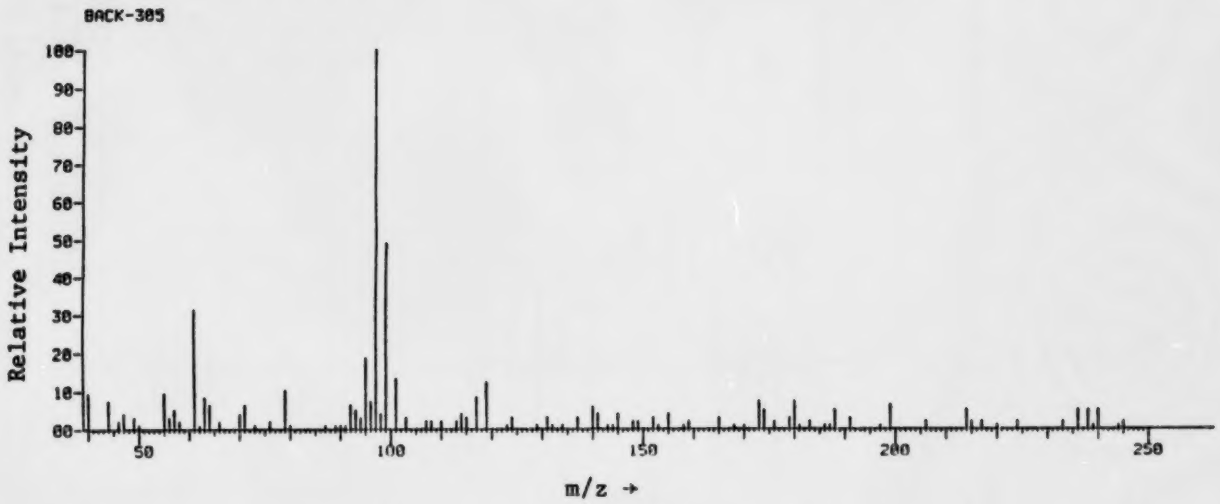


Figure A8. Mass spectrum of peak at 10.33 min.

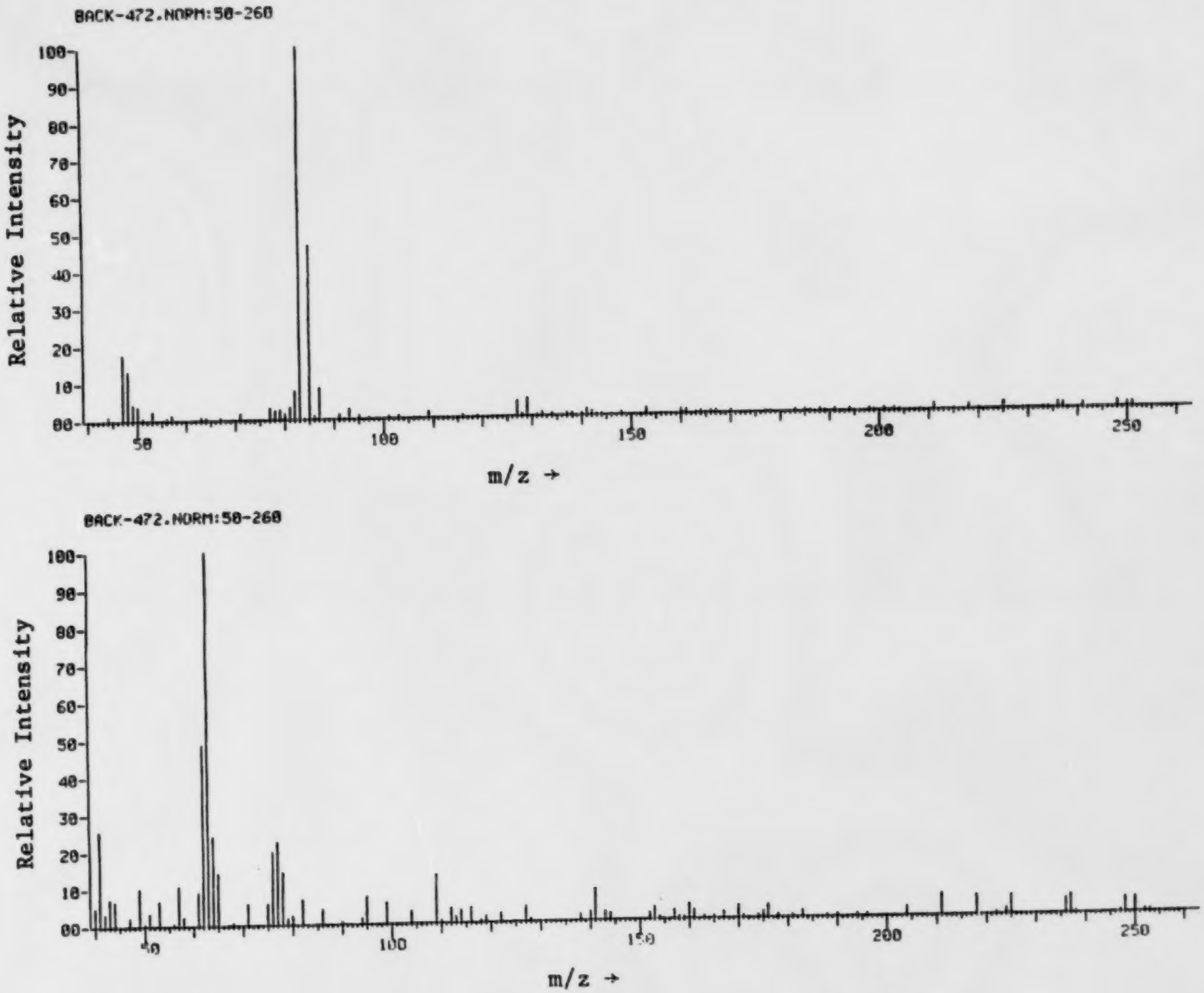


Figure A9. Mass spectra of peaks at 12.46 and 13.19 min.

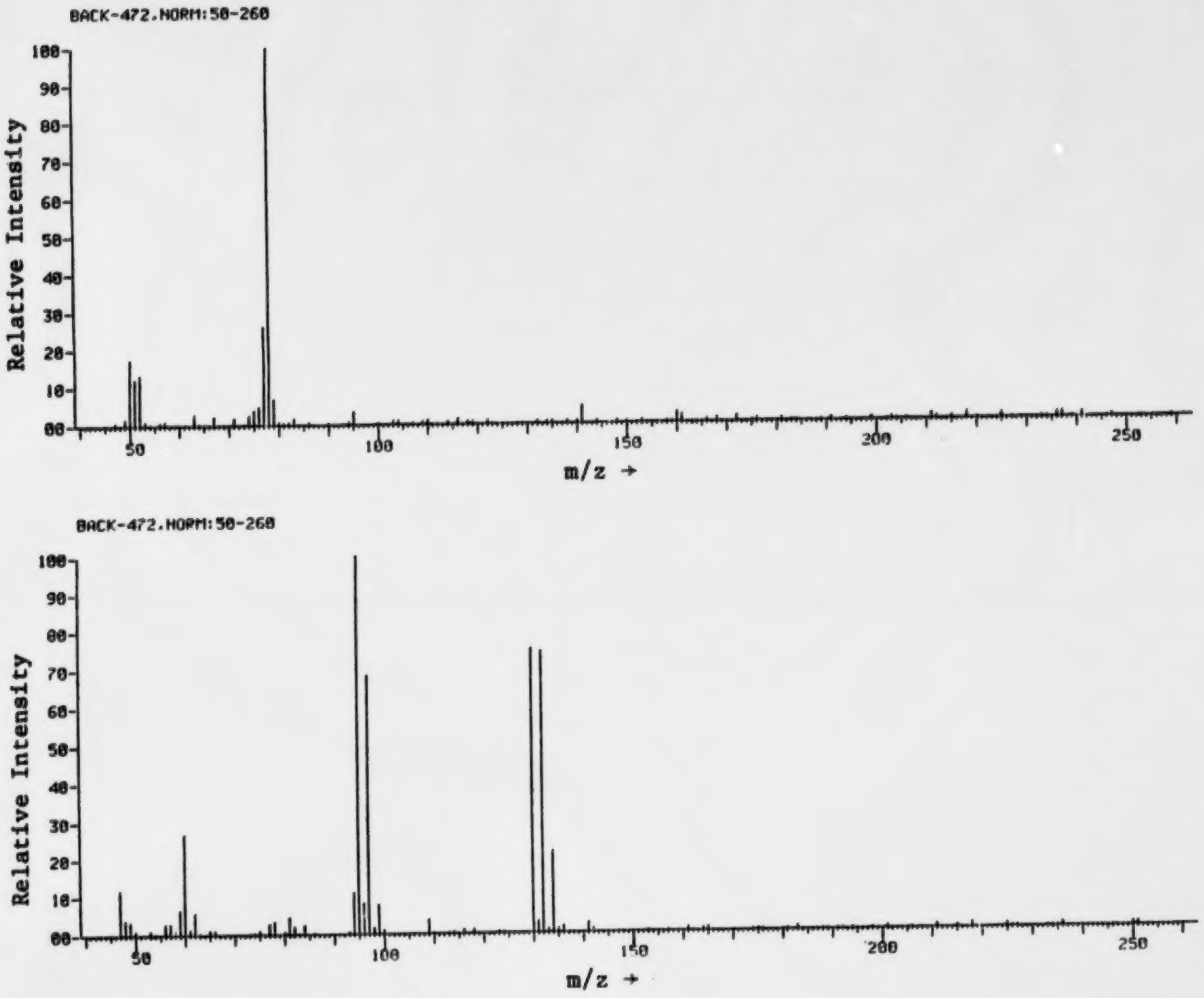


Figure A10. Mass spectra of peaks at 13.53 and 13.93 min.

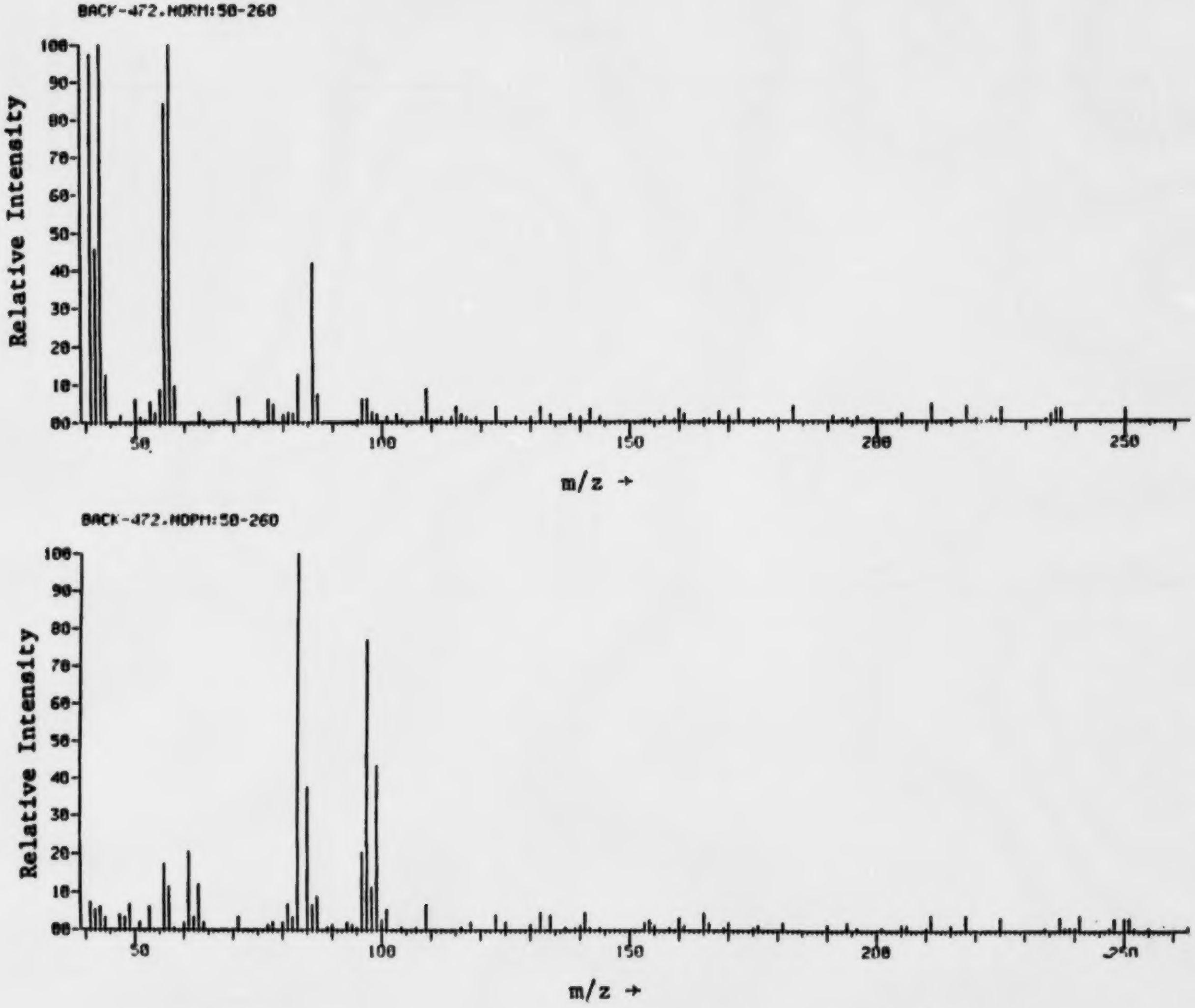


Figure A11. Mass spectra of peaks at 15.09 and 15.26 min.

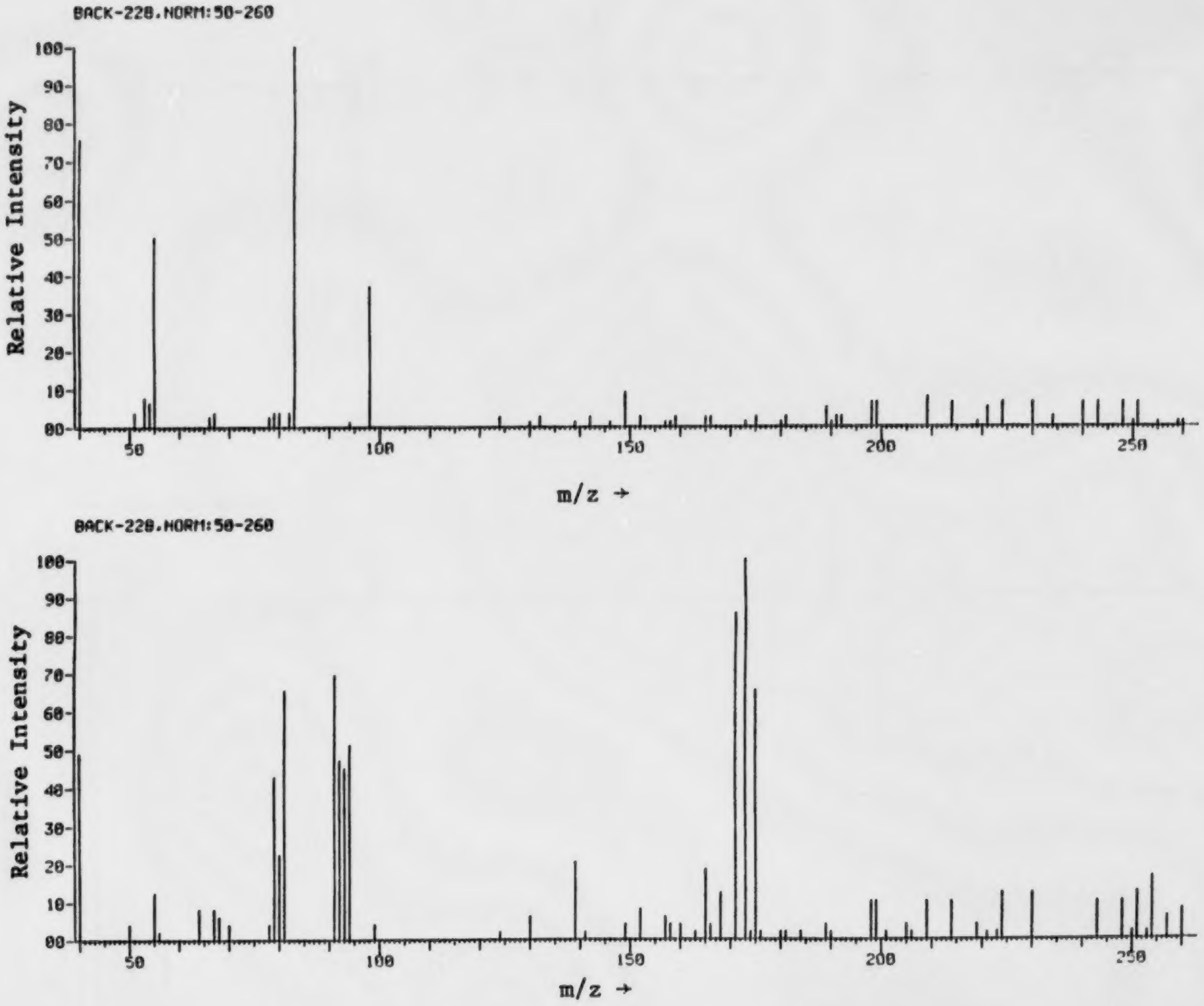


Figure A12. Mass spectra of peaks at 16.19 and 18.03 min.

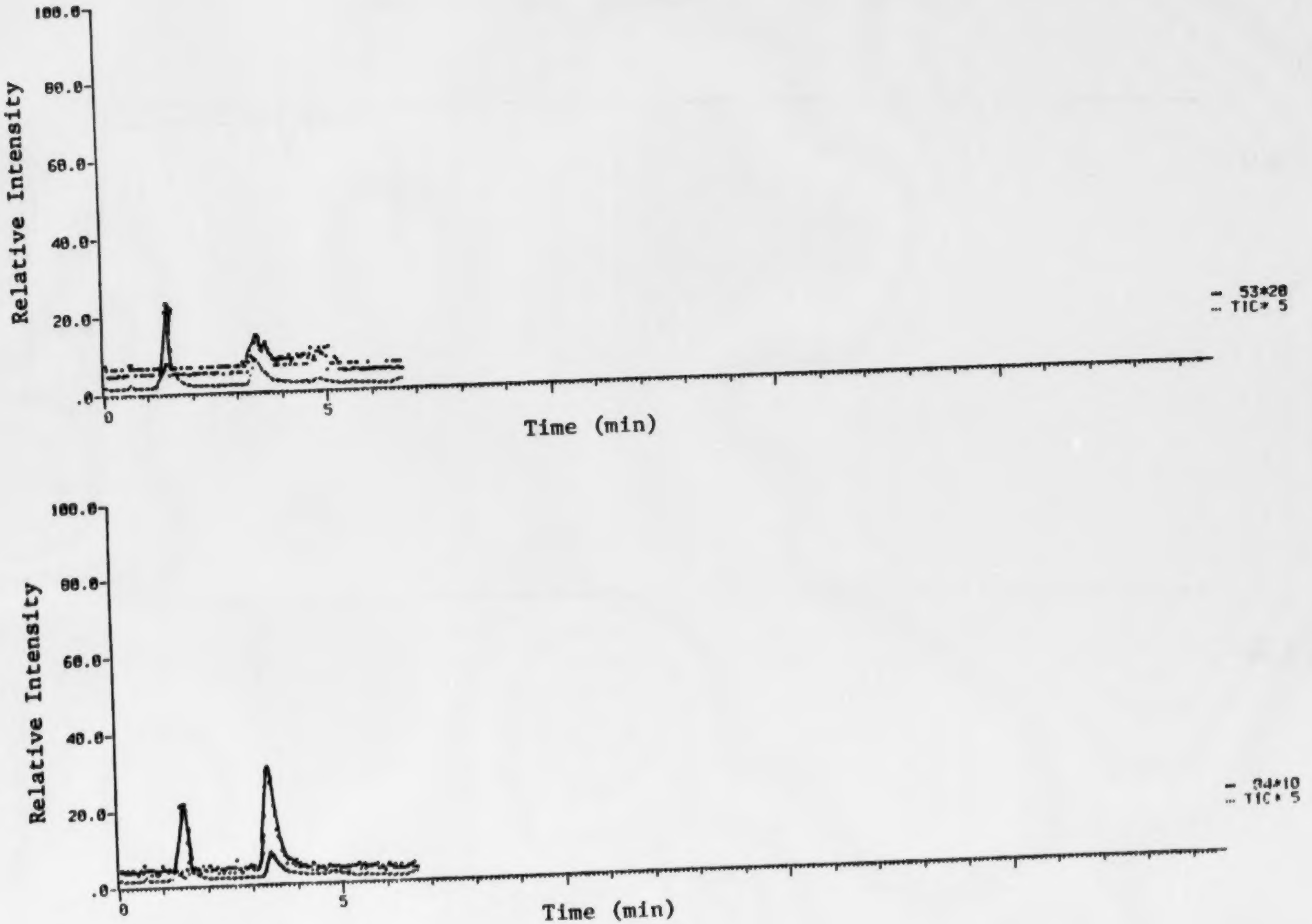


Figure A13. Mass chromatograms - m/z 53, 84.

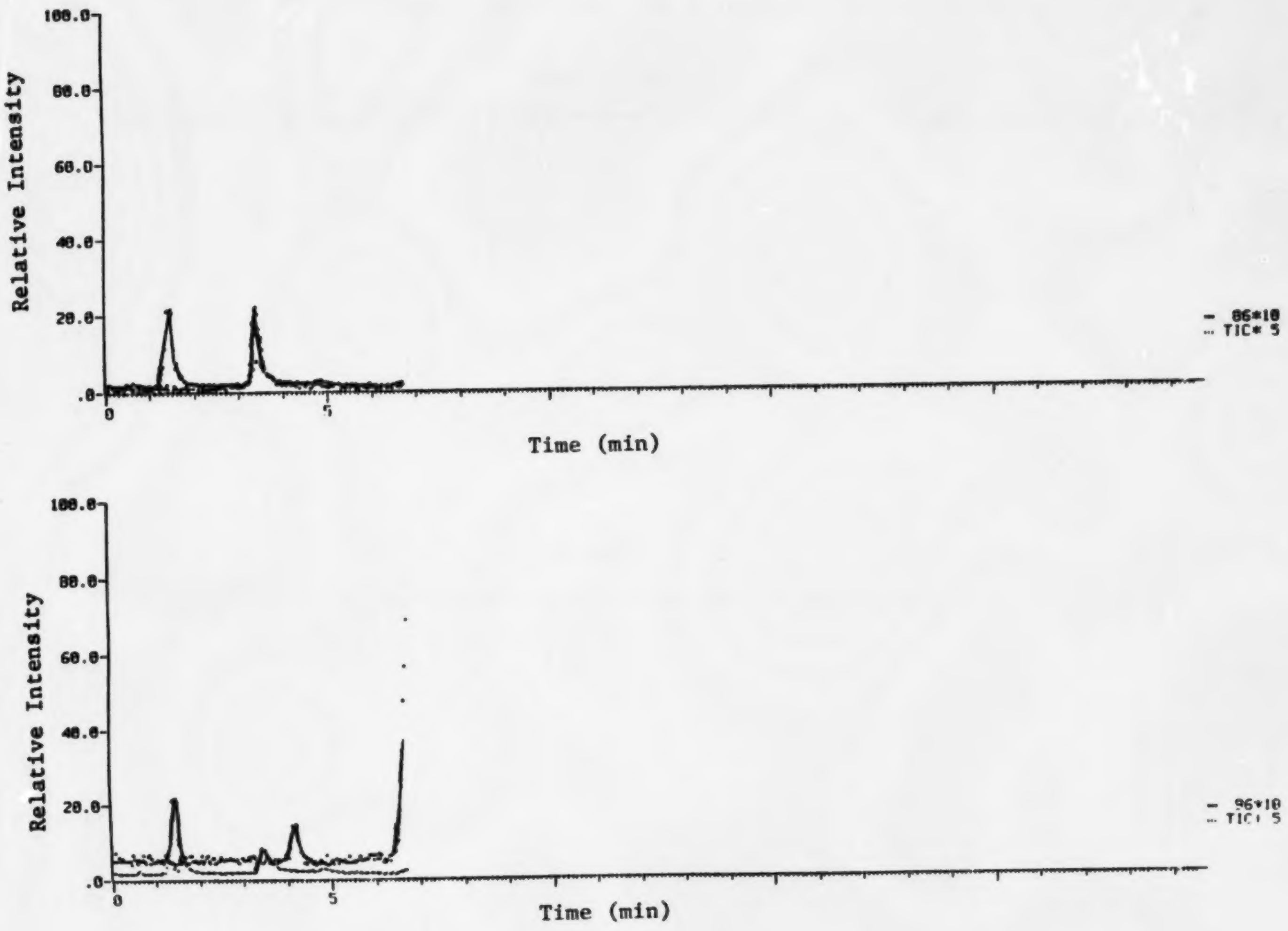


Figure A14. Mass chromatograms - m/z 86, 96.

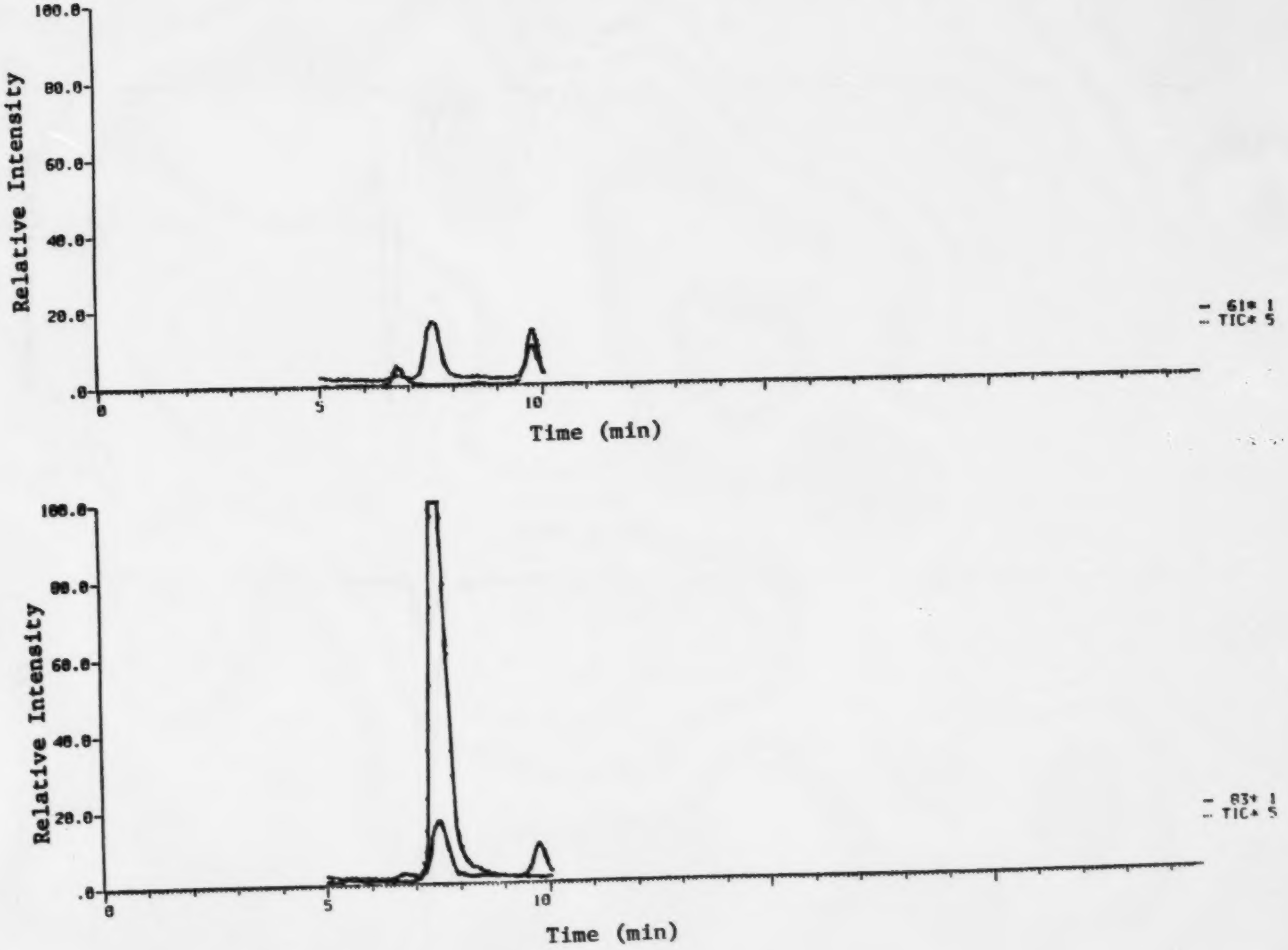


Figure A15. Mass chromatograms - m/z 61, 83.

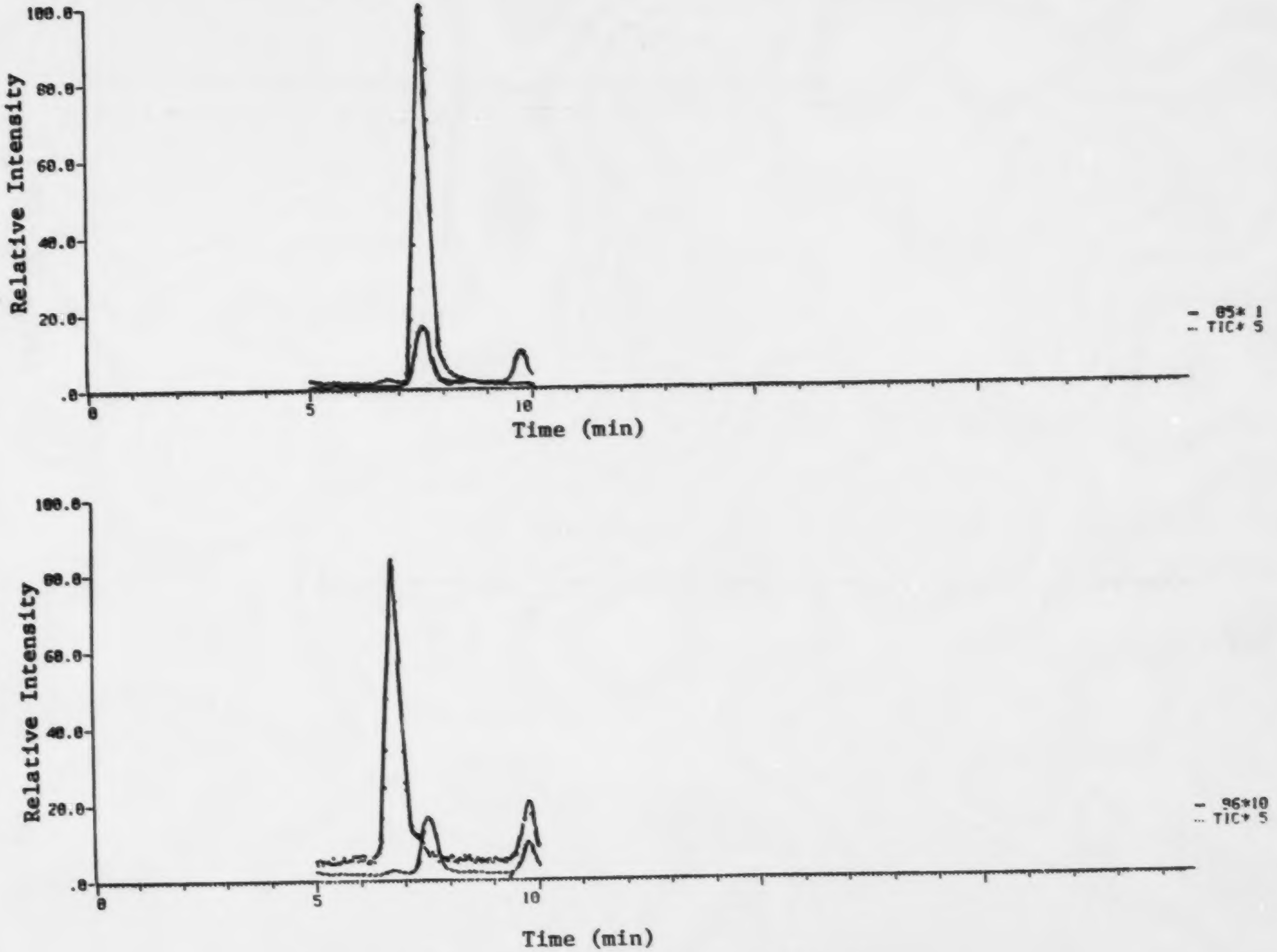


Figure A16. Mass chromatograms - m/z 85, 96.

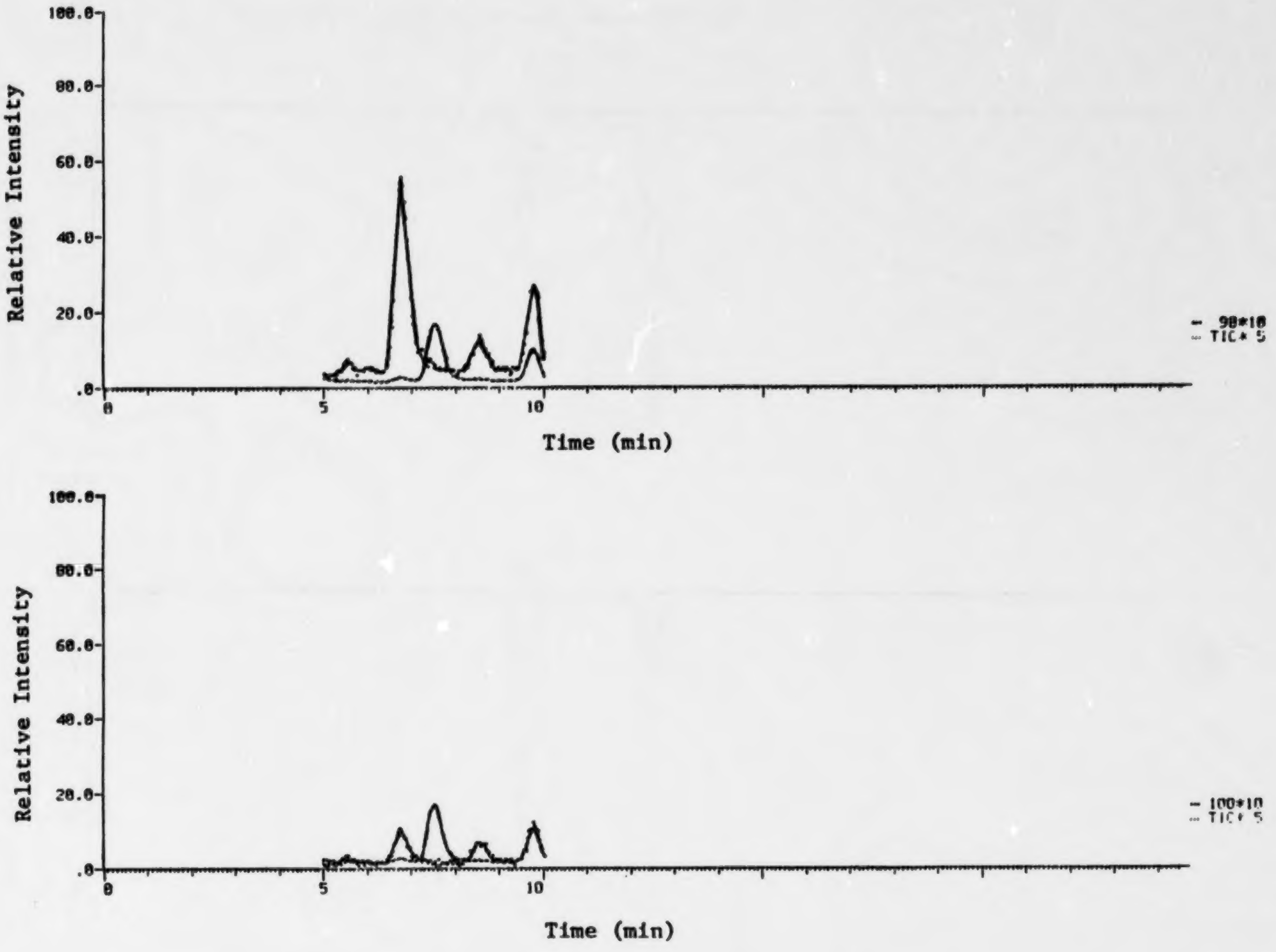


Figure A17. Mass chromatograms - m/z 98, 100

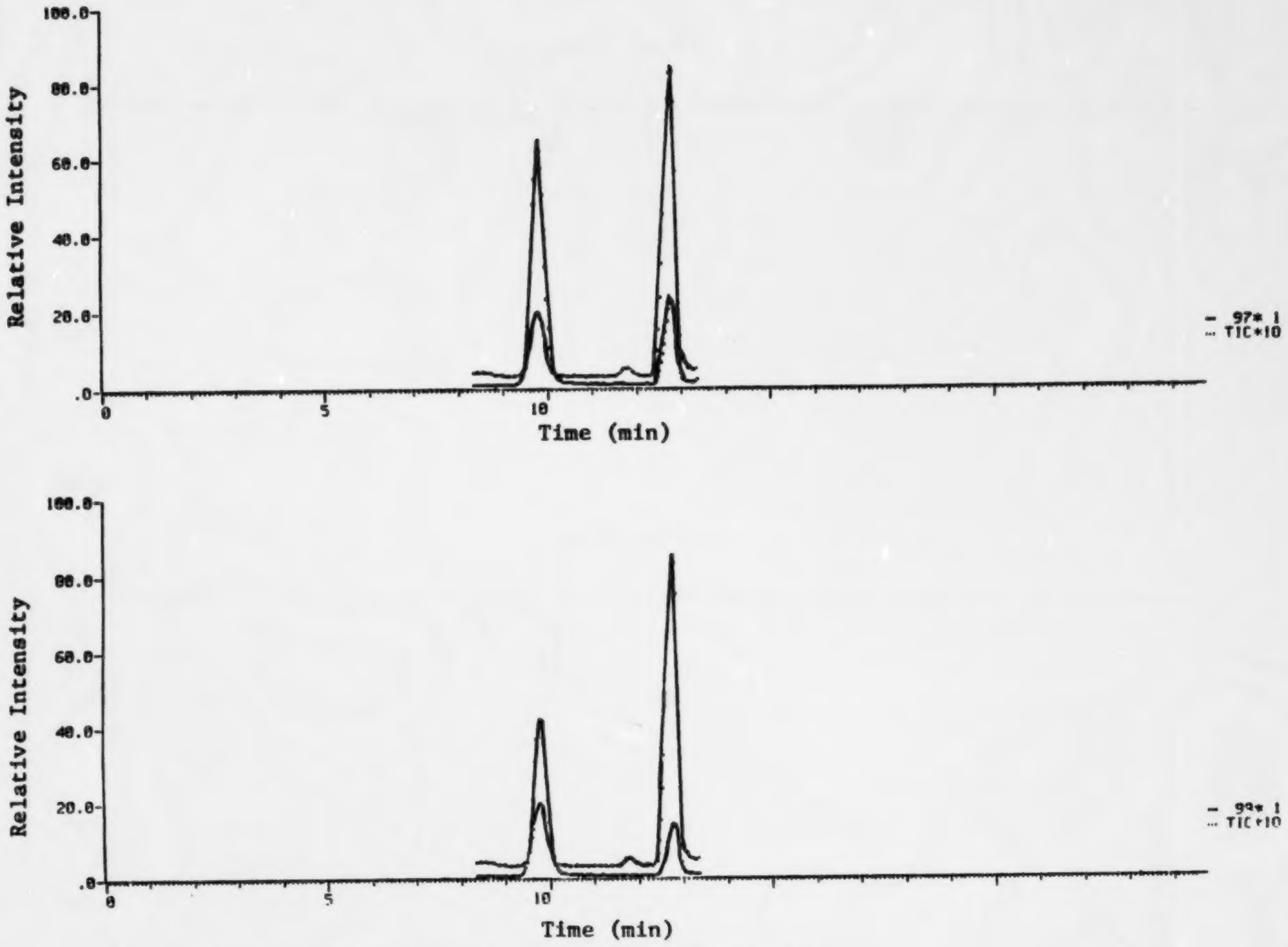


Figure A18. Mass chromatograms - m/z 97, 99.

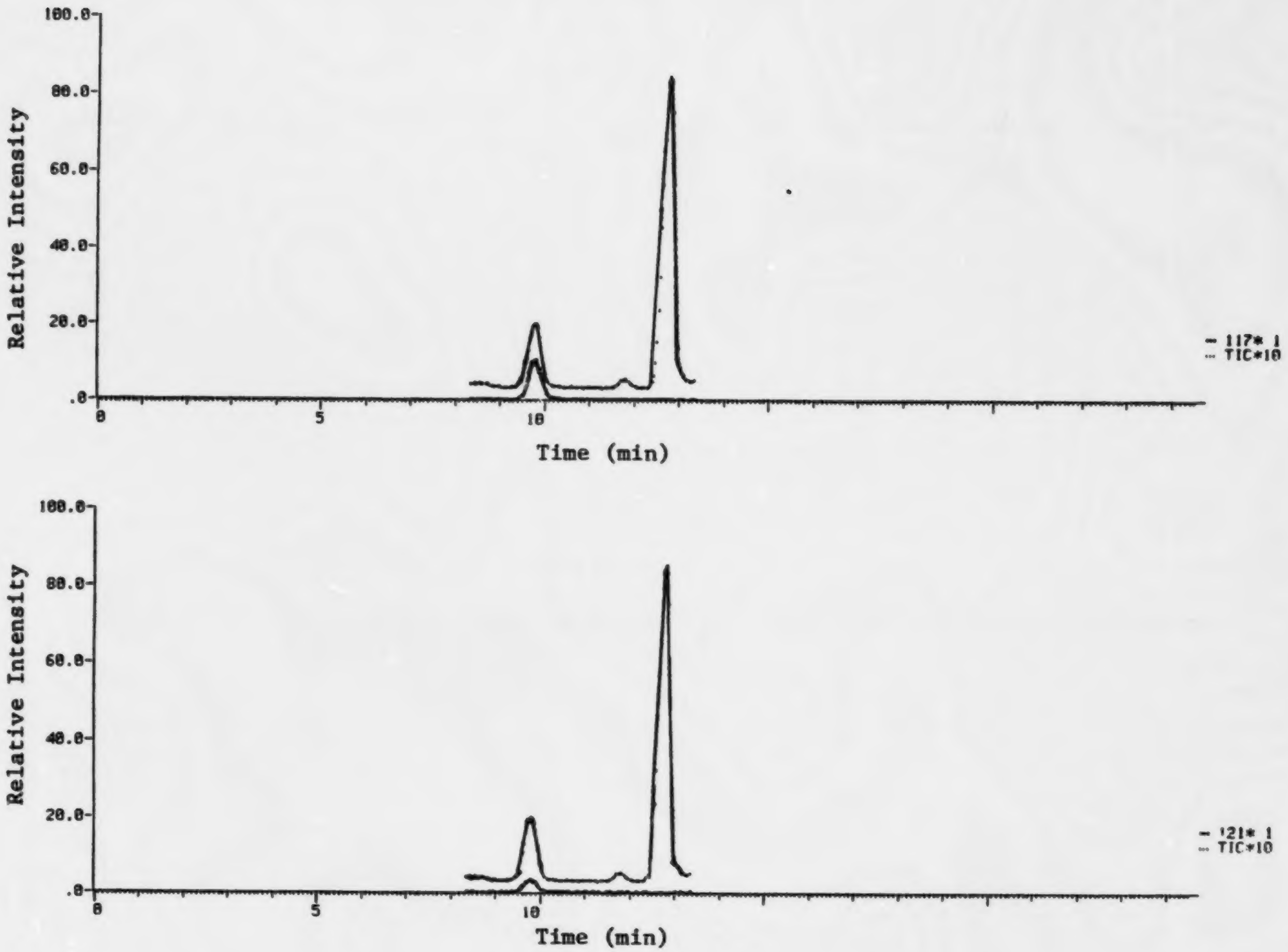


Figure A19. Mass chromatograms - m/z 117, 121

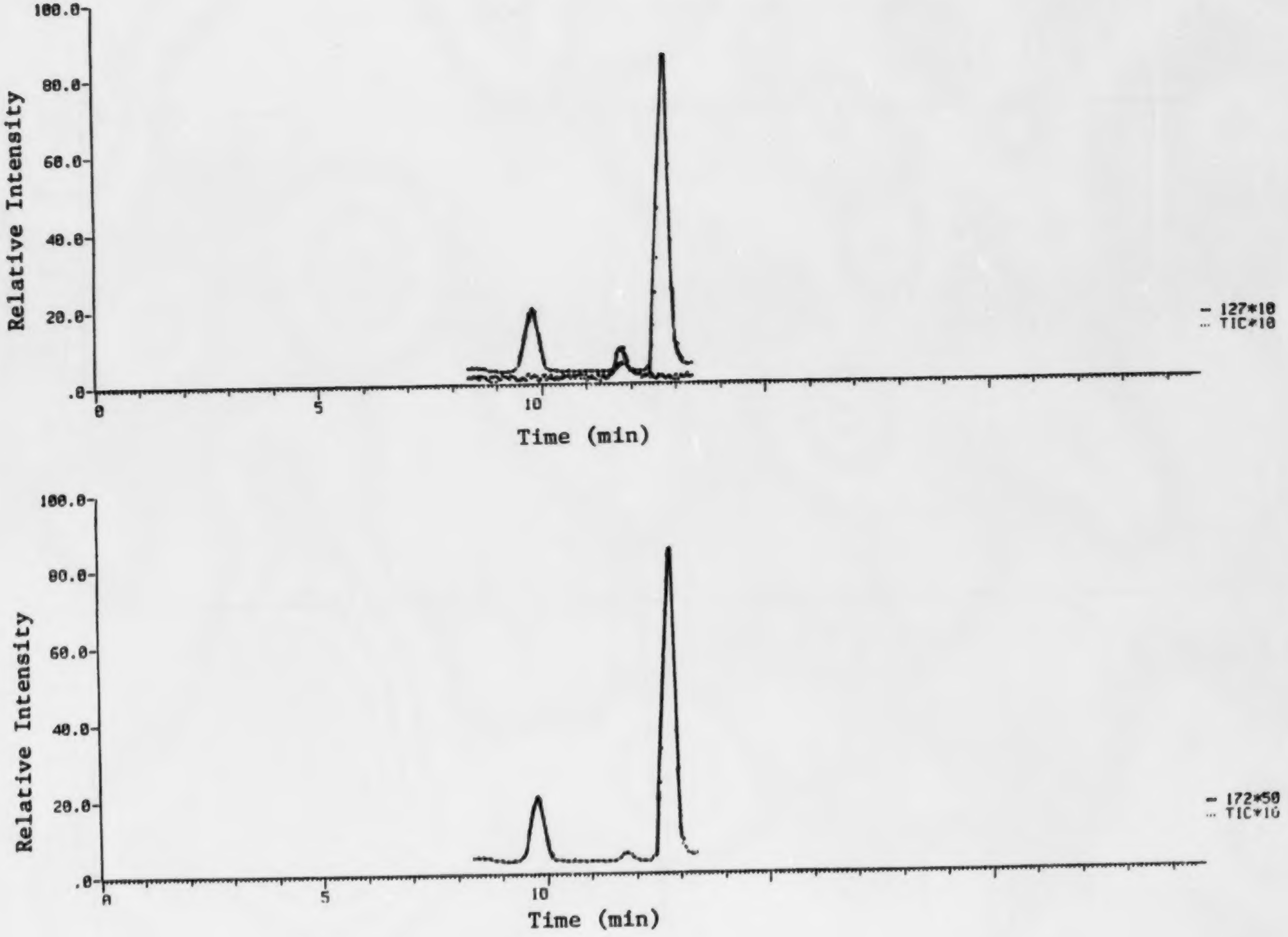


Figure A20. Mass chromatograms - m/z 127, 172

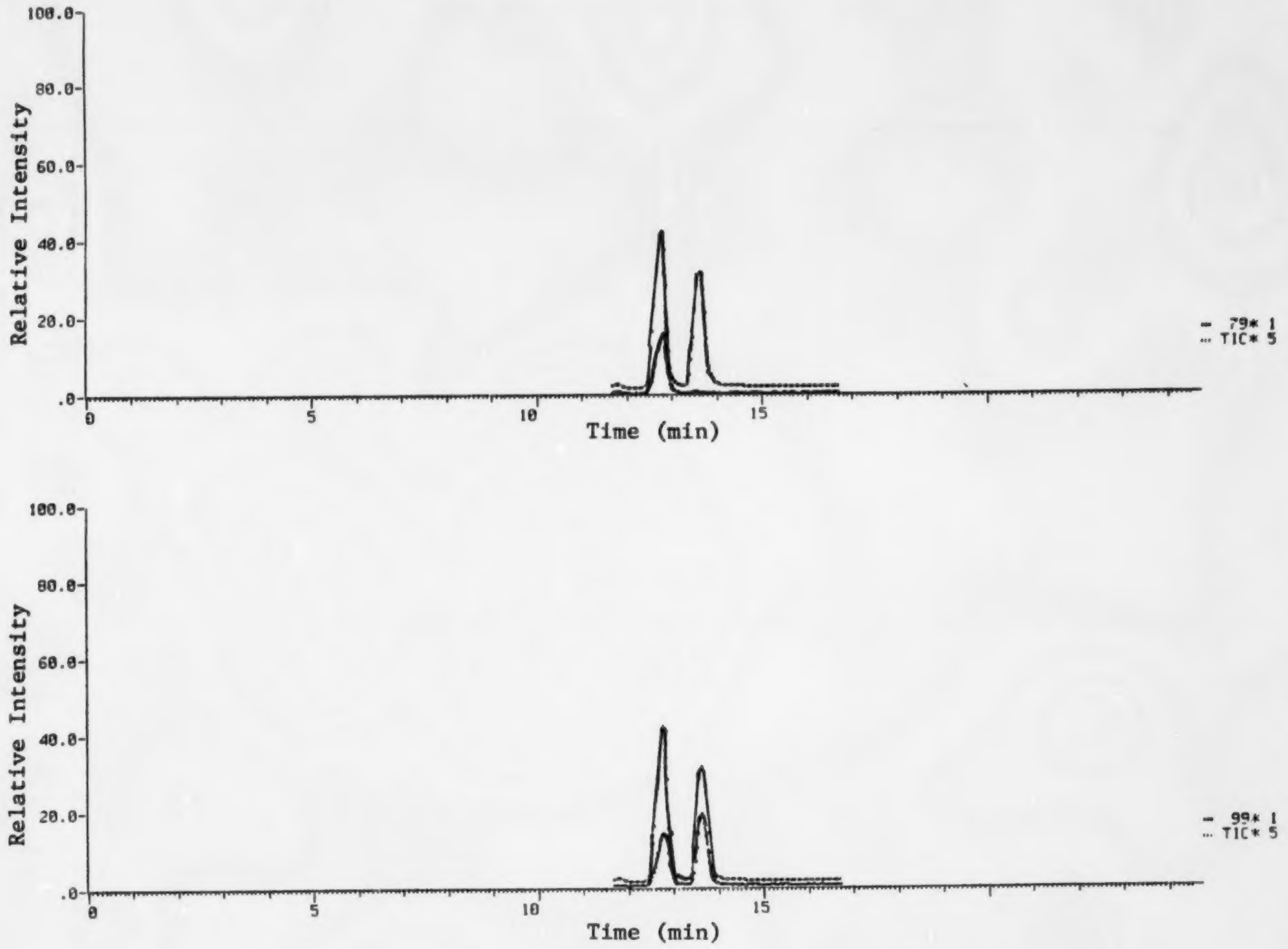


Figure A21. Mass chromatograms - m/z 79, 99.

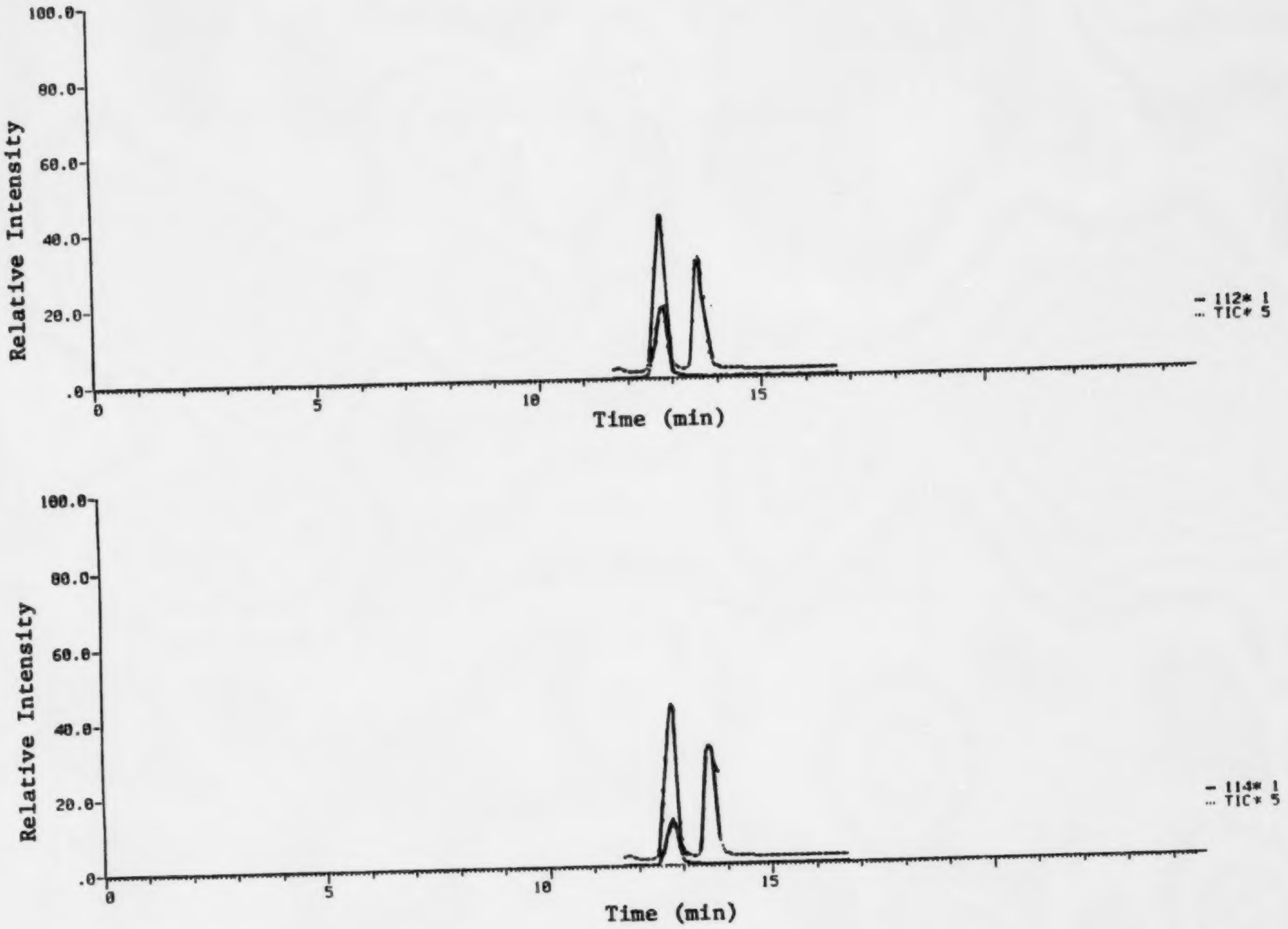


Figure A22. Mass chromatograms - m/z 112, 114.

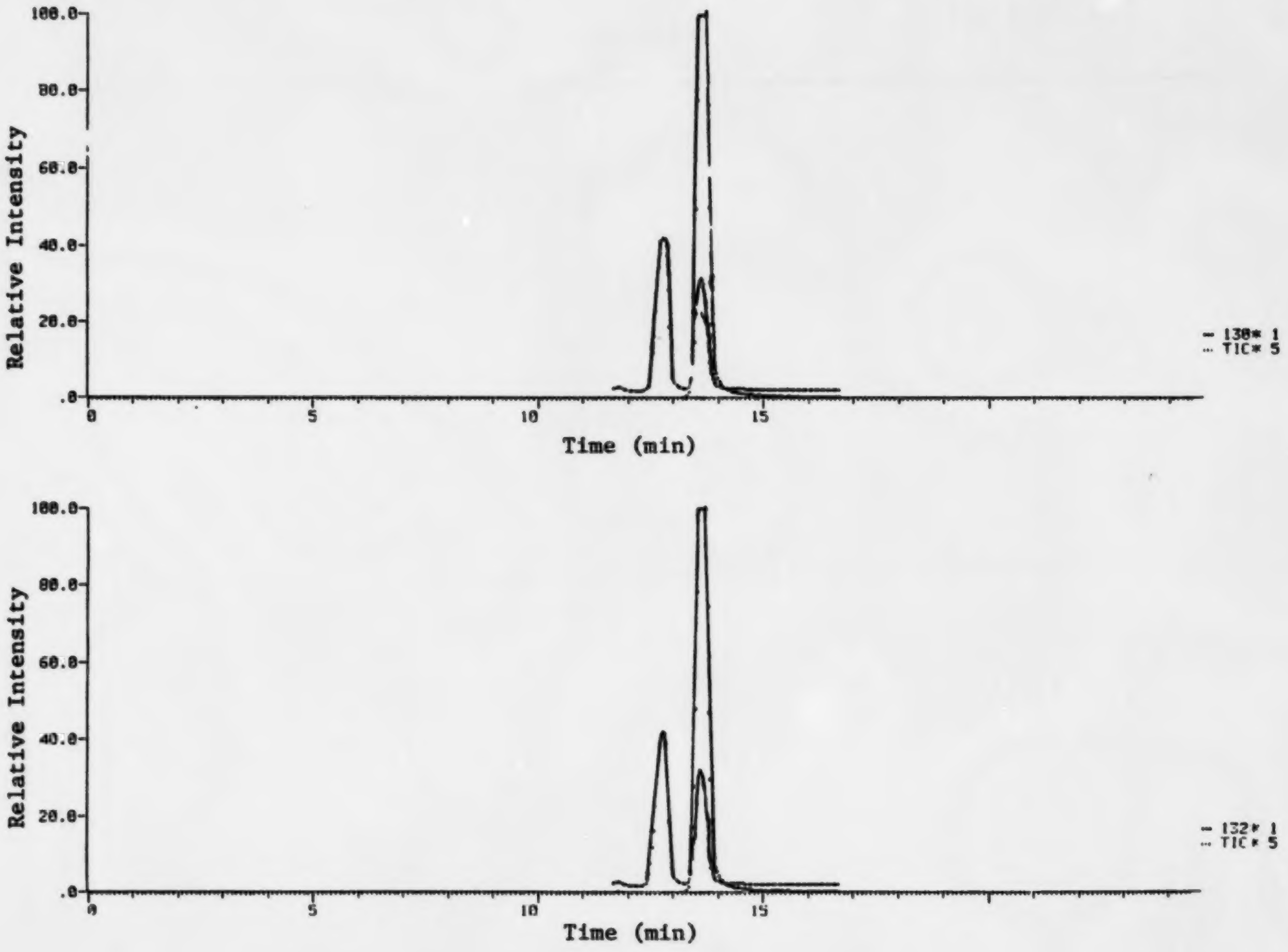


Figure A23. Mass chromatograms - m/z 130, 132.

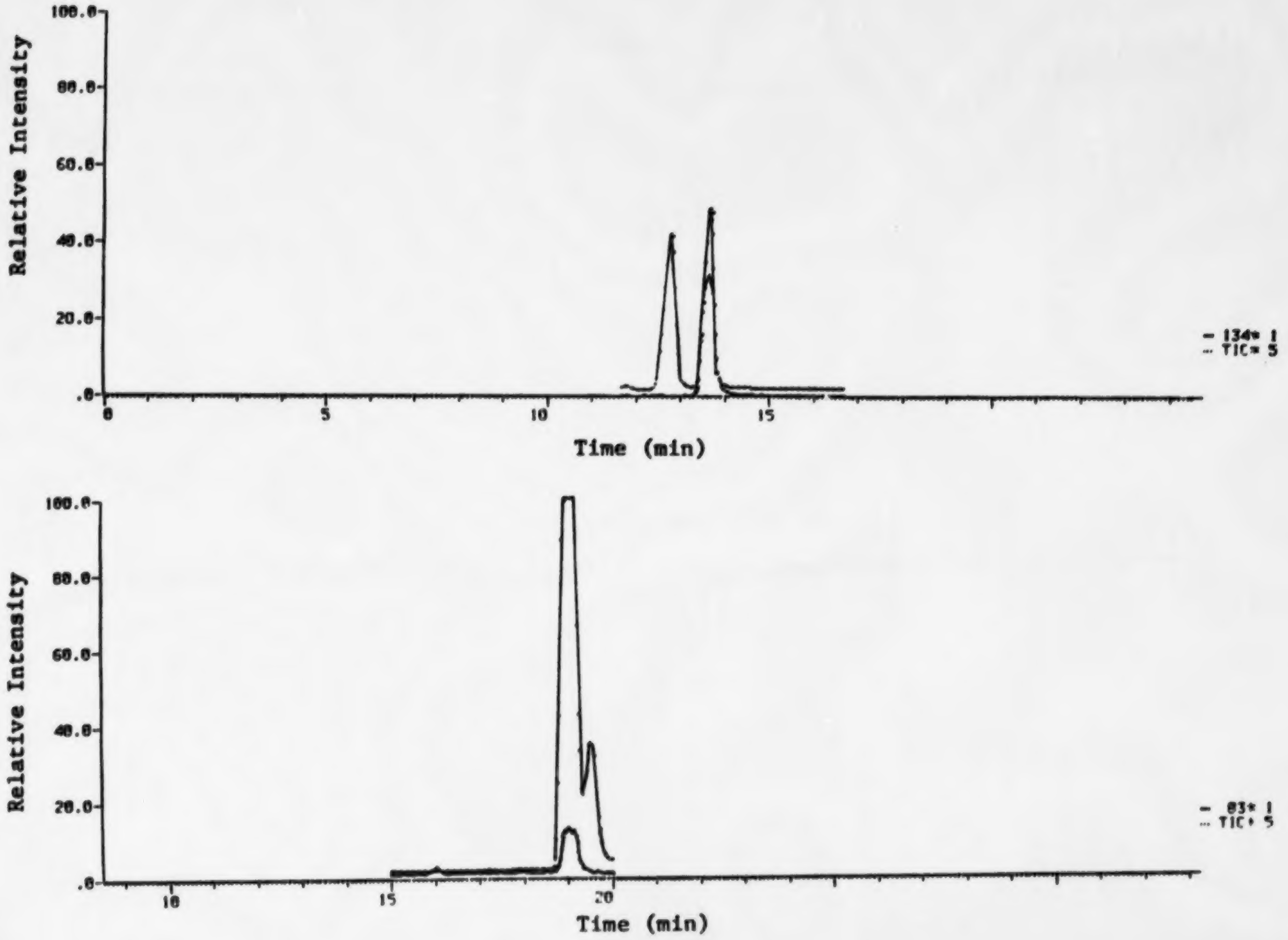


Figure A24. Mass chromatograms - m/z 134, 83.

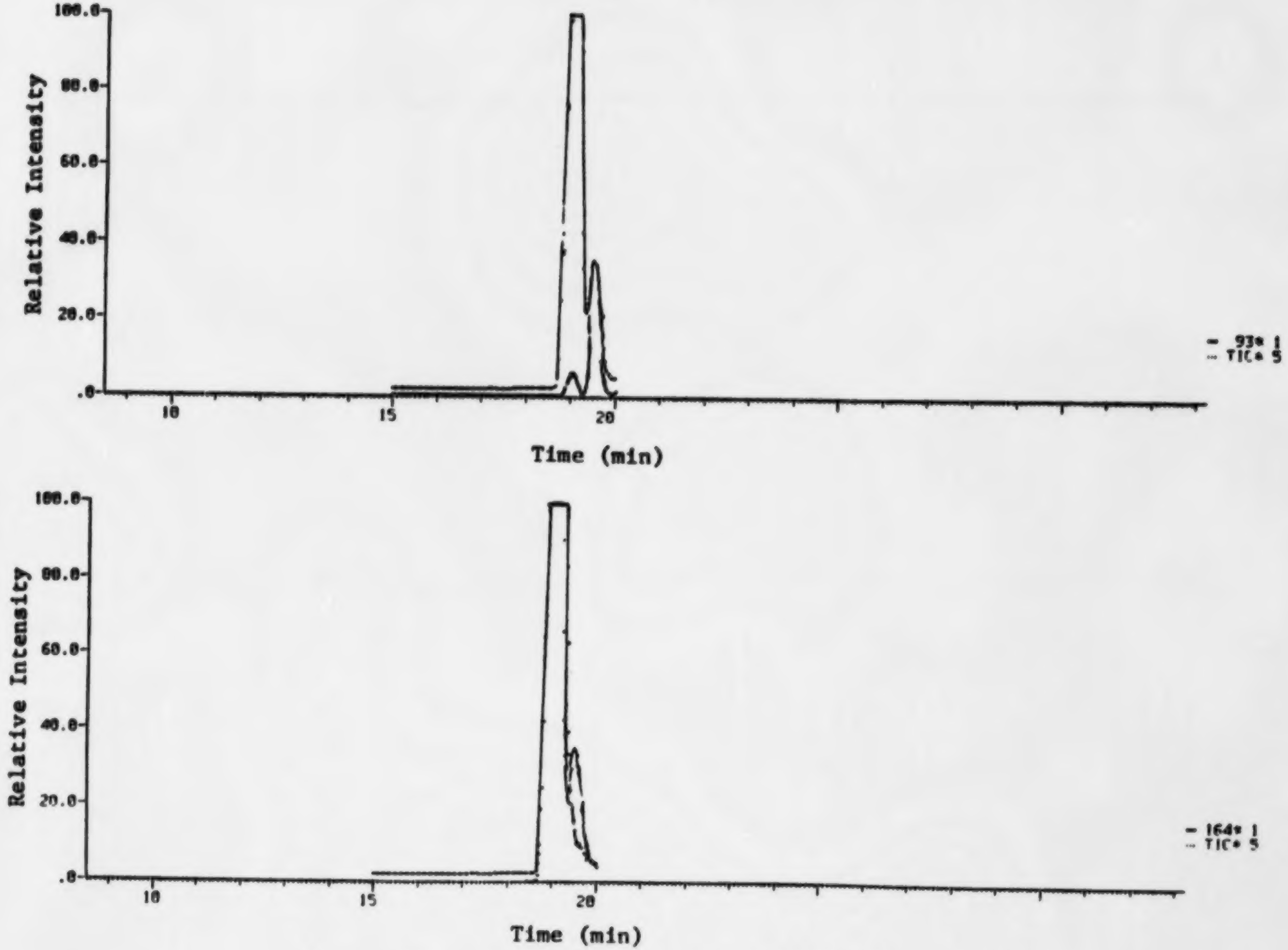


Figure A25. Mass chromatograms - m/z 93, 164.

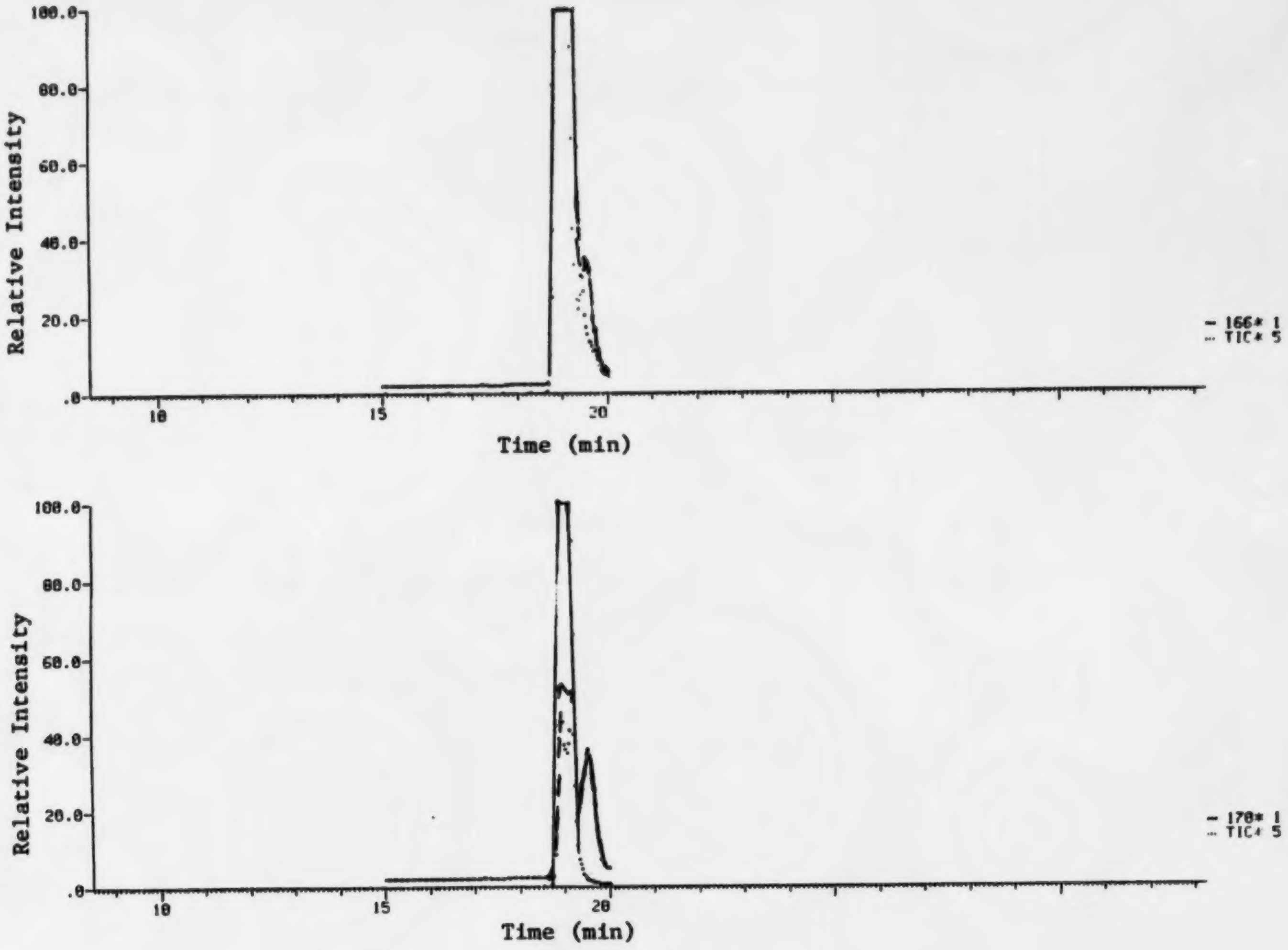


Figure A26. Mass chromatograms - m/z 166, 170.

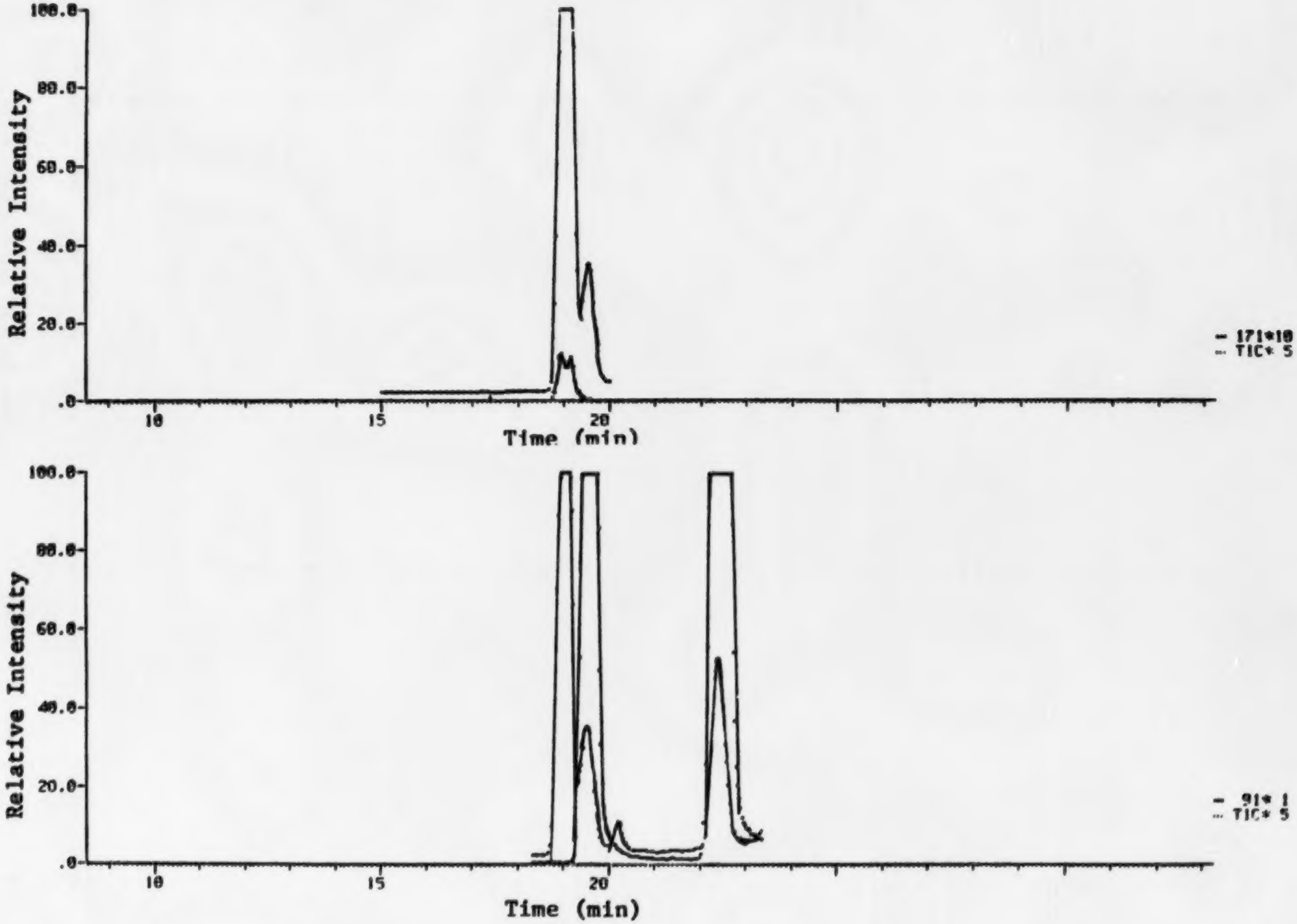


Figure A27. Mass chromatograms - m/z 171, 91.

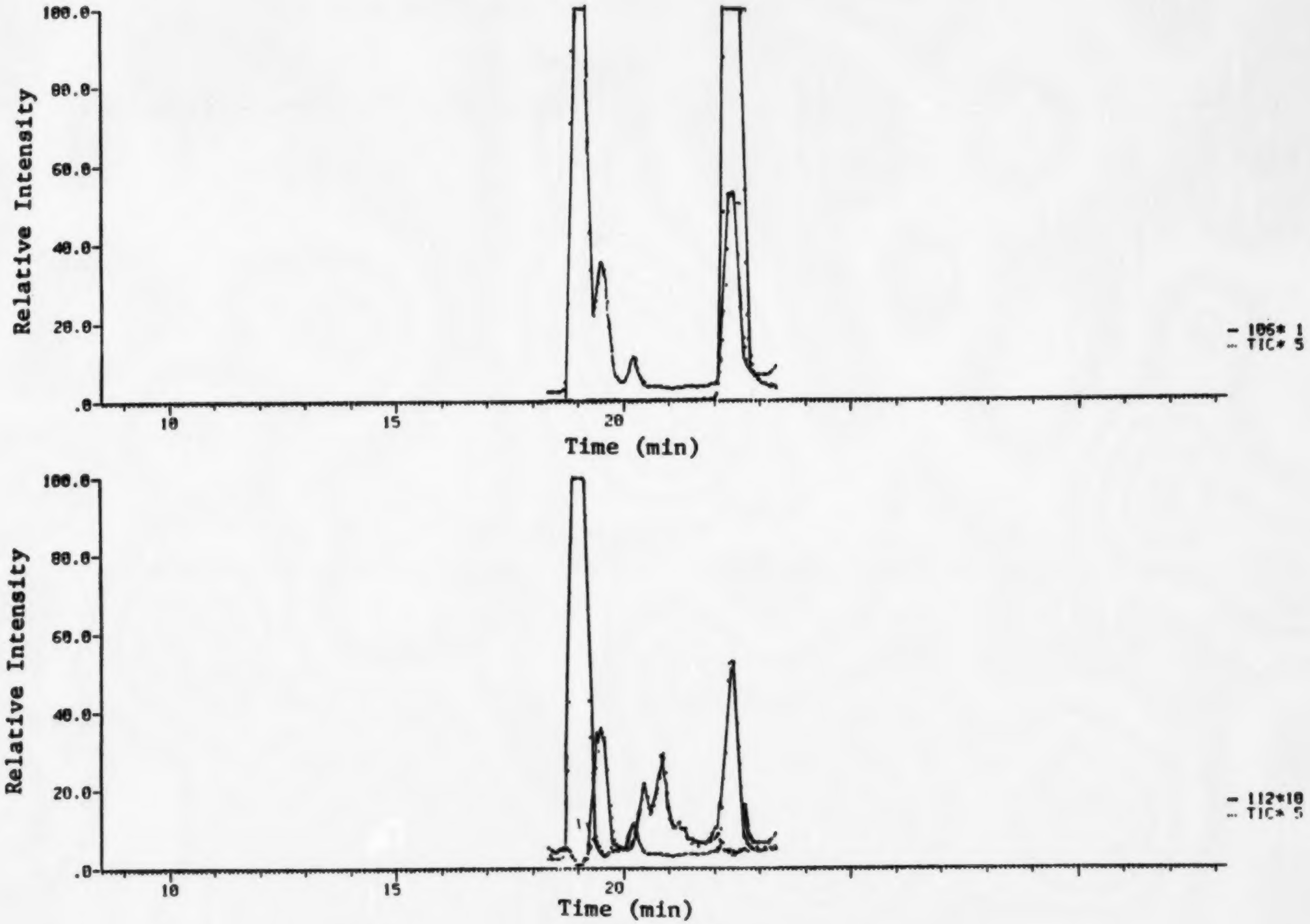


Figure A28. Mass chromatograms - m/z 106, 112.

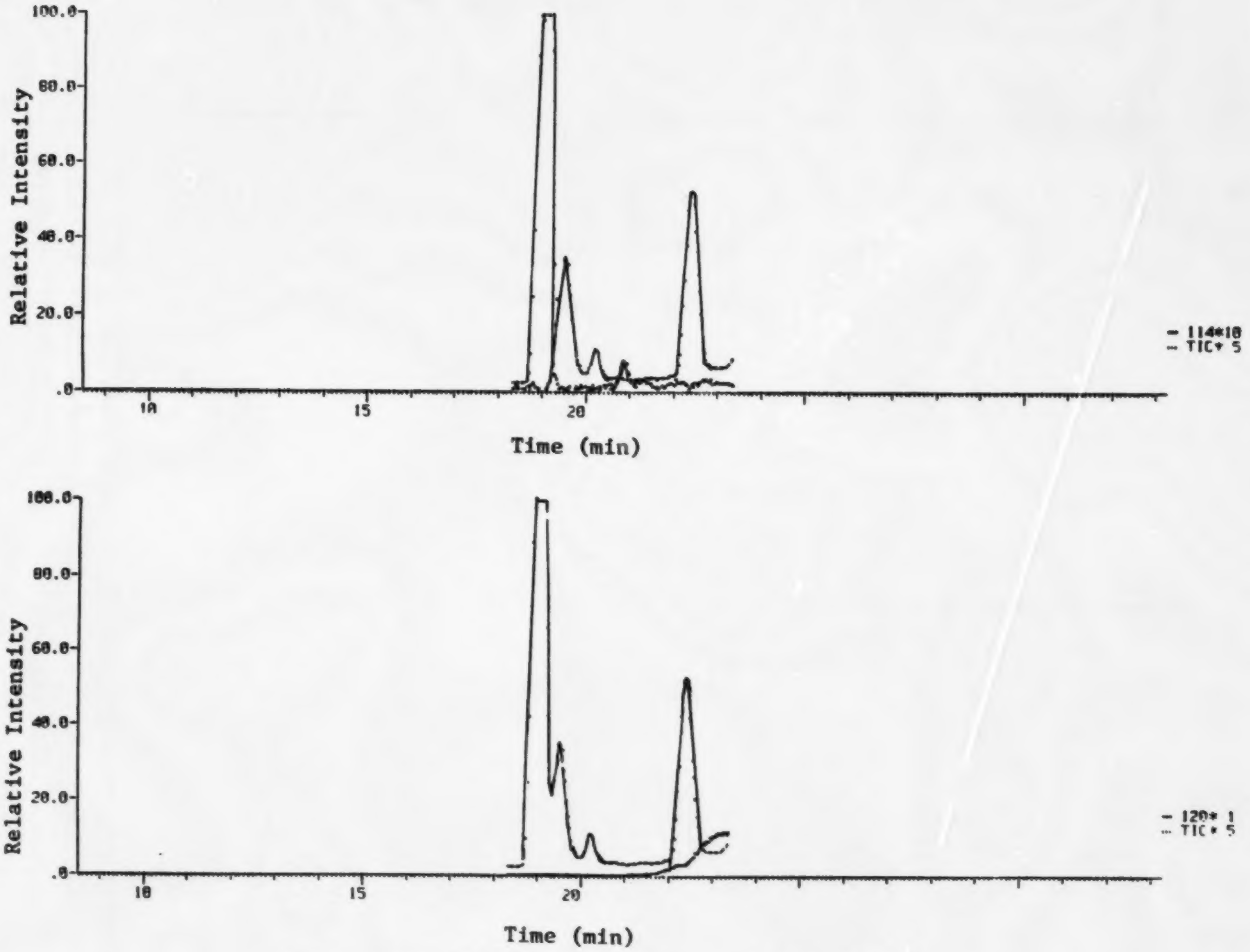


Figure A29. Mass chromatograms - m/z 114, 120.

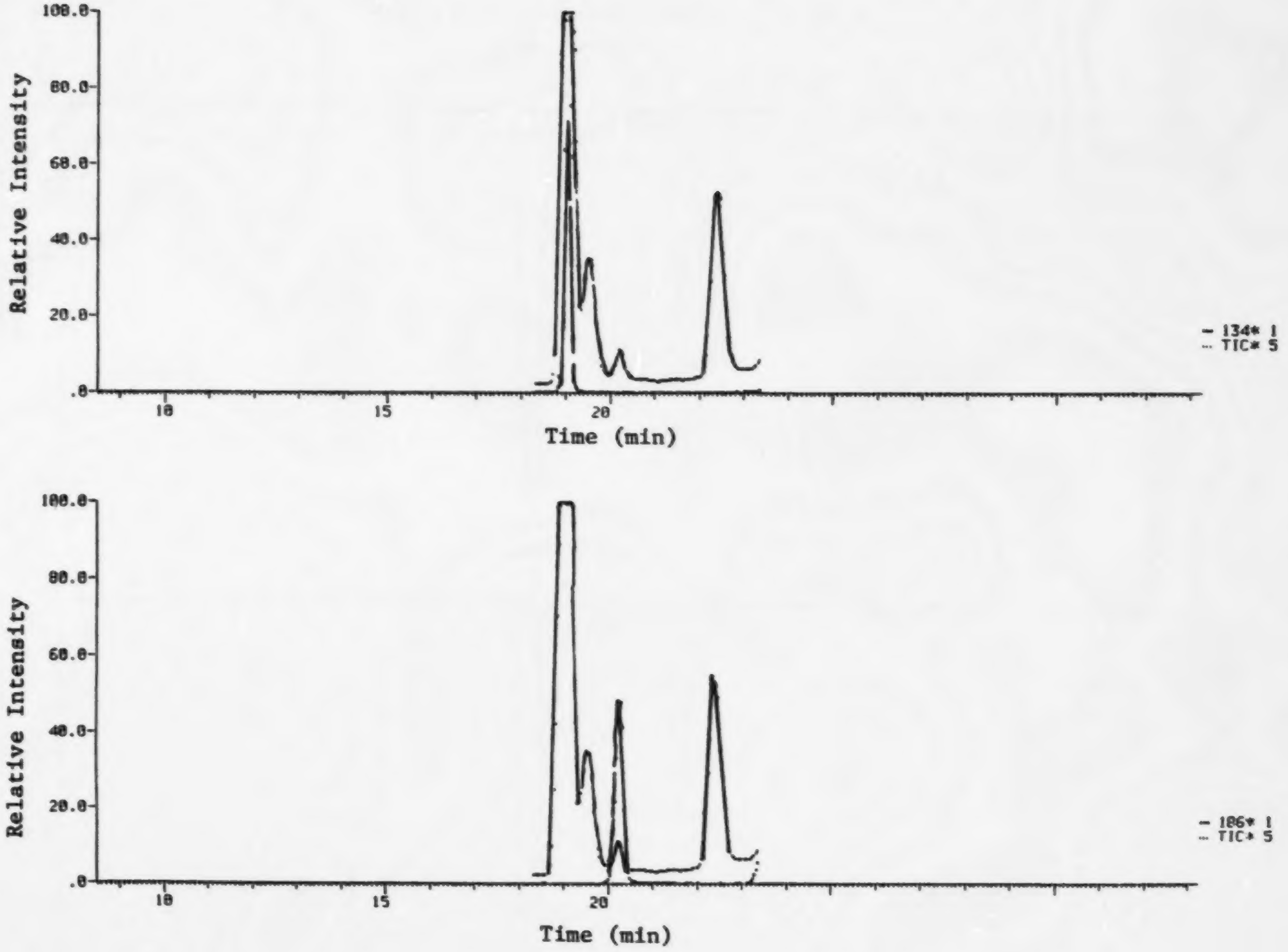


Figure A30. Mass chromatograms - m/z 134, 186

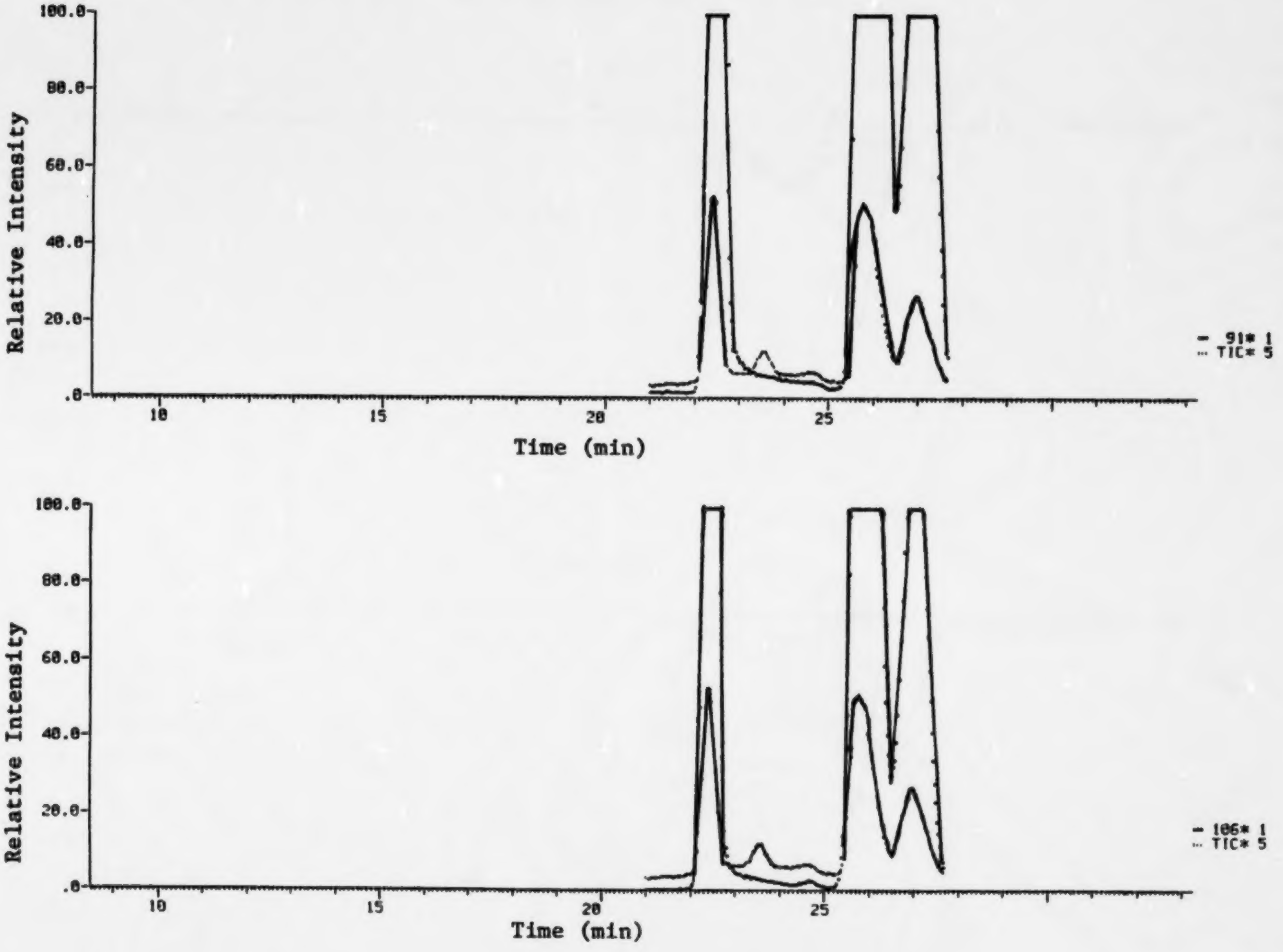


Figure A31. Mass chromatograms - m/z 91, 106

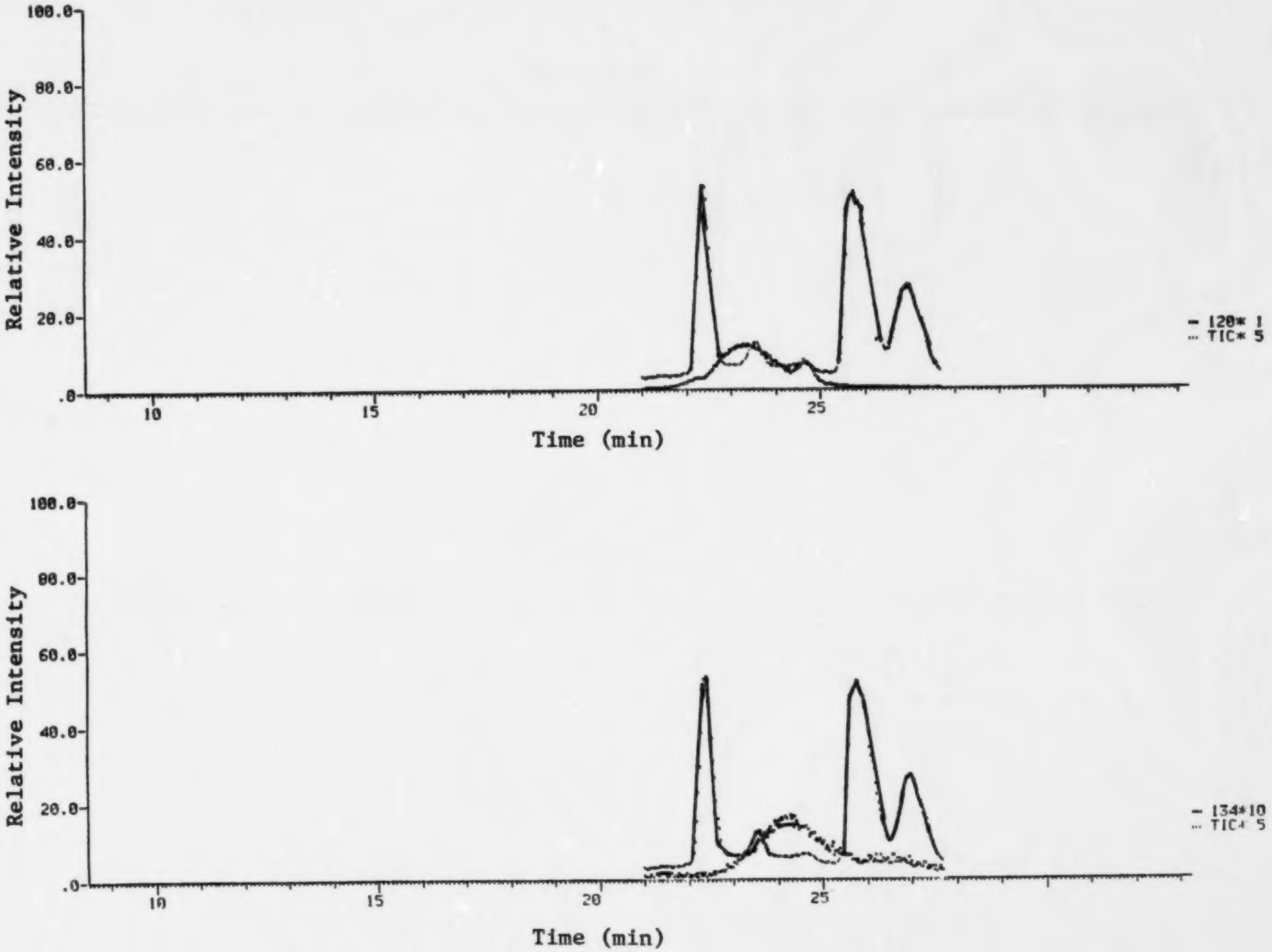


Figure A32. Mass chromatograms - m/z 120, 134

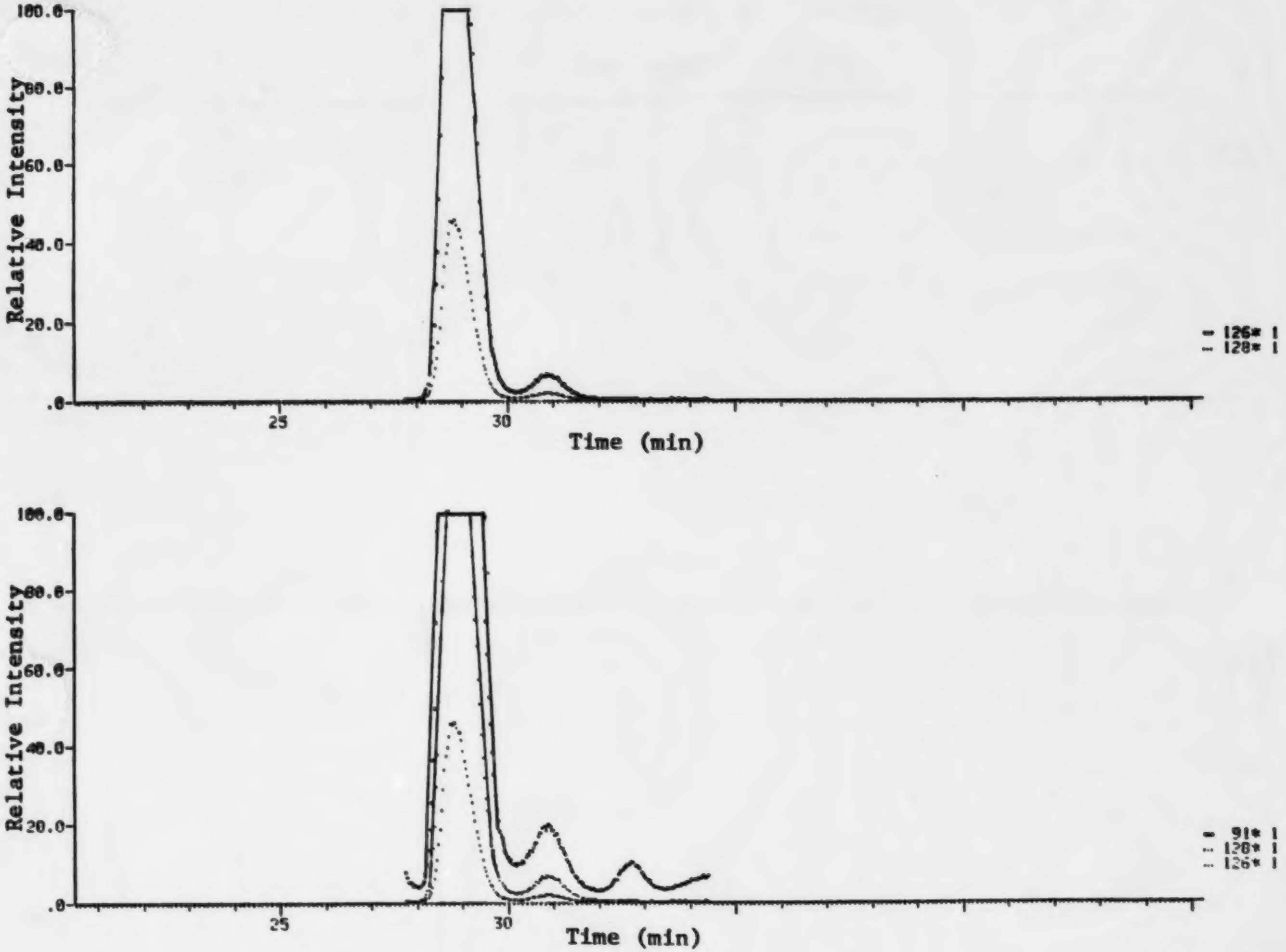
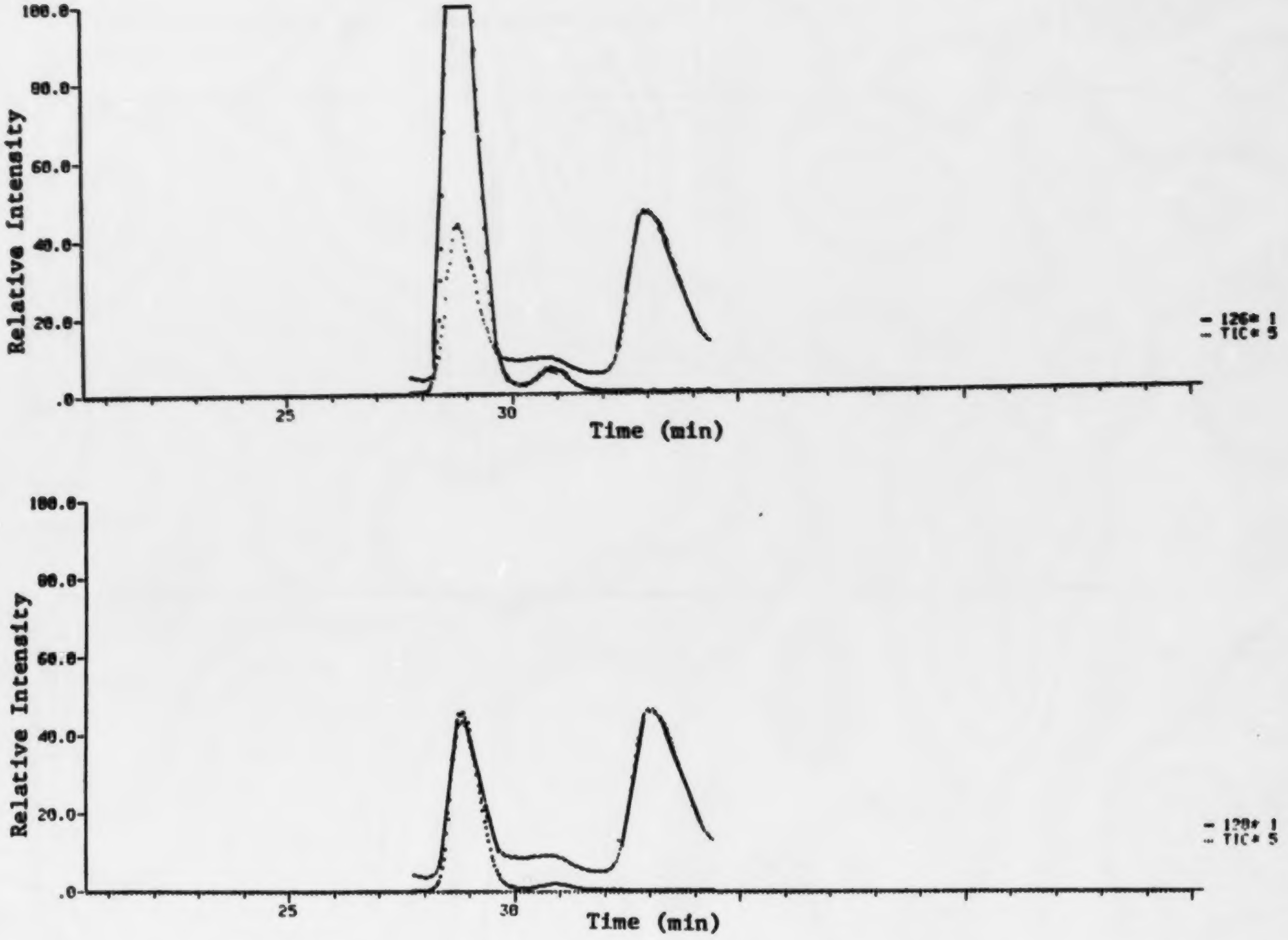


Figure A33. Mass chromatograms - m/z 126, 91.



igure A34. Mass chromatograms - m/z 126, 128.

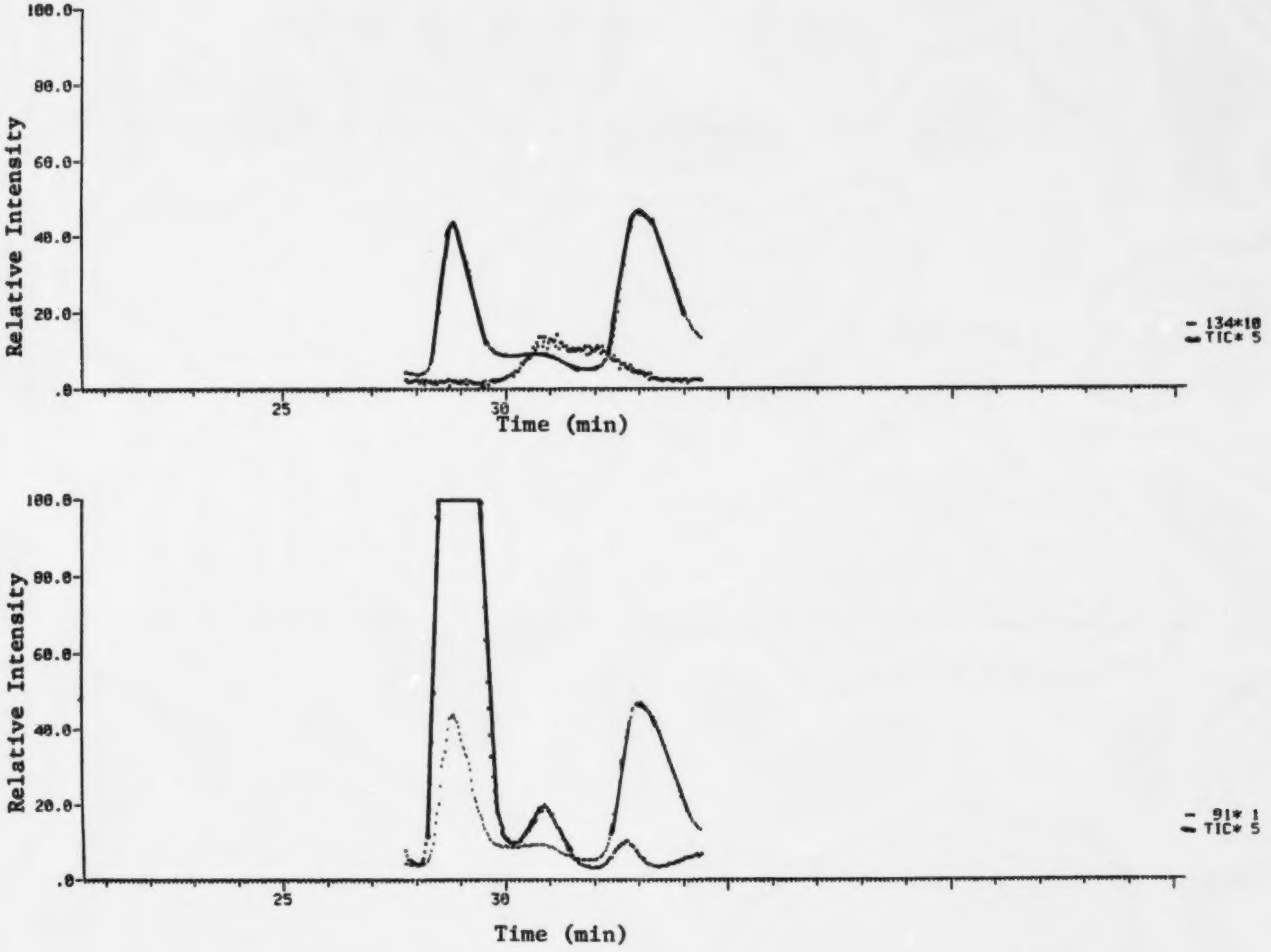


Figure A35. Mass chromatograms - m/z 134, 91.

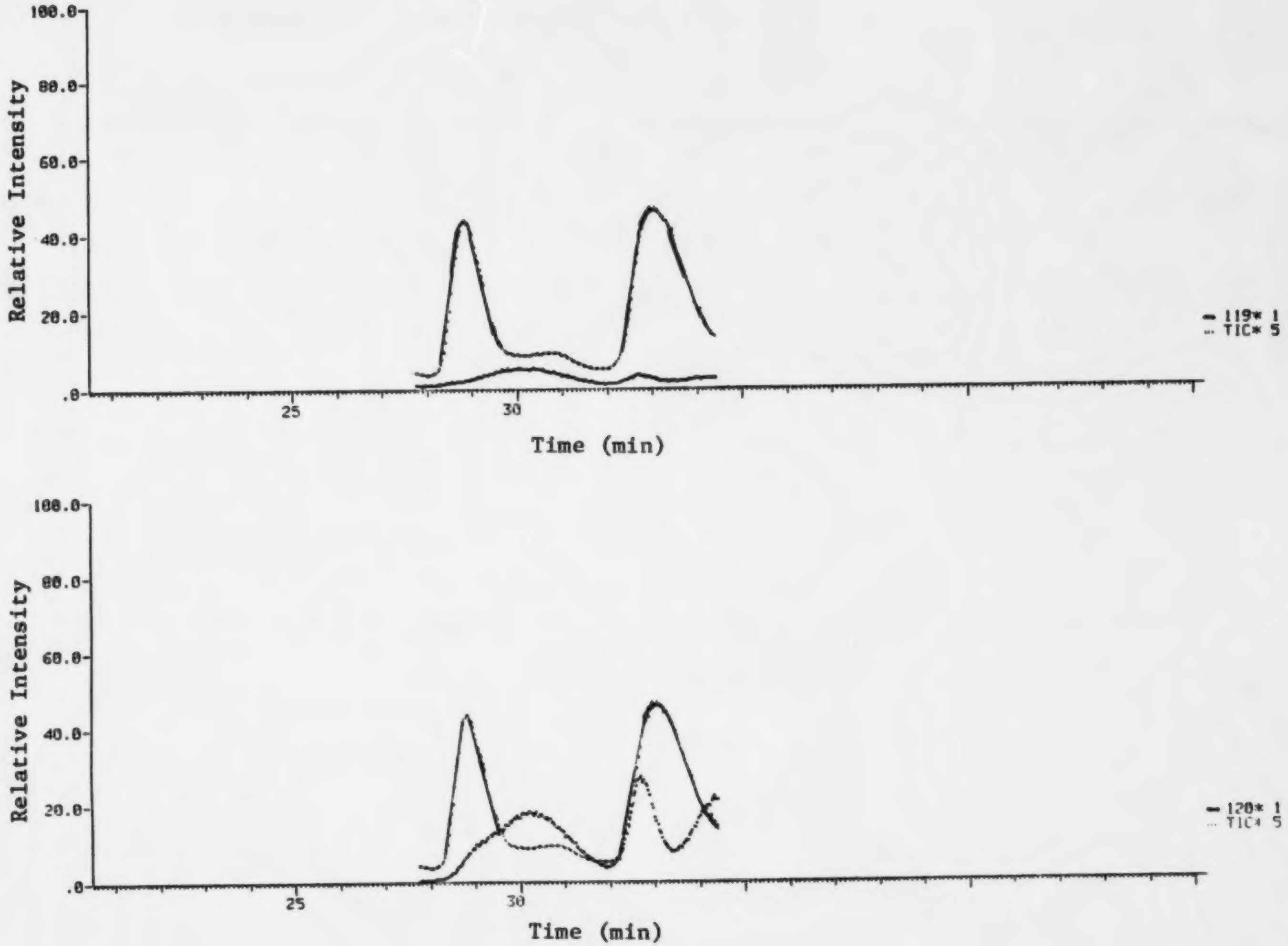


Figure A36. Mass chromatograms - m/z 119, 120.

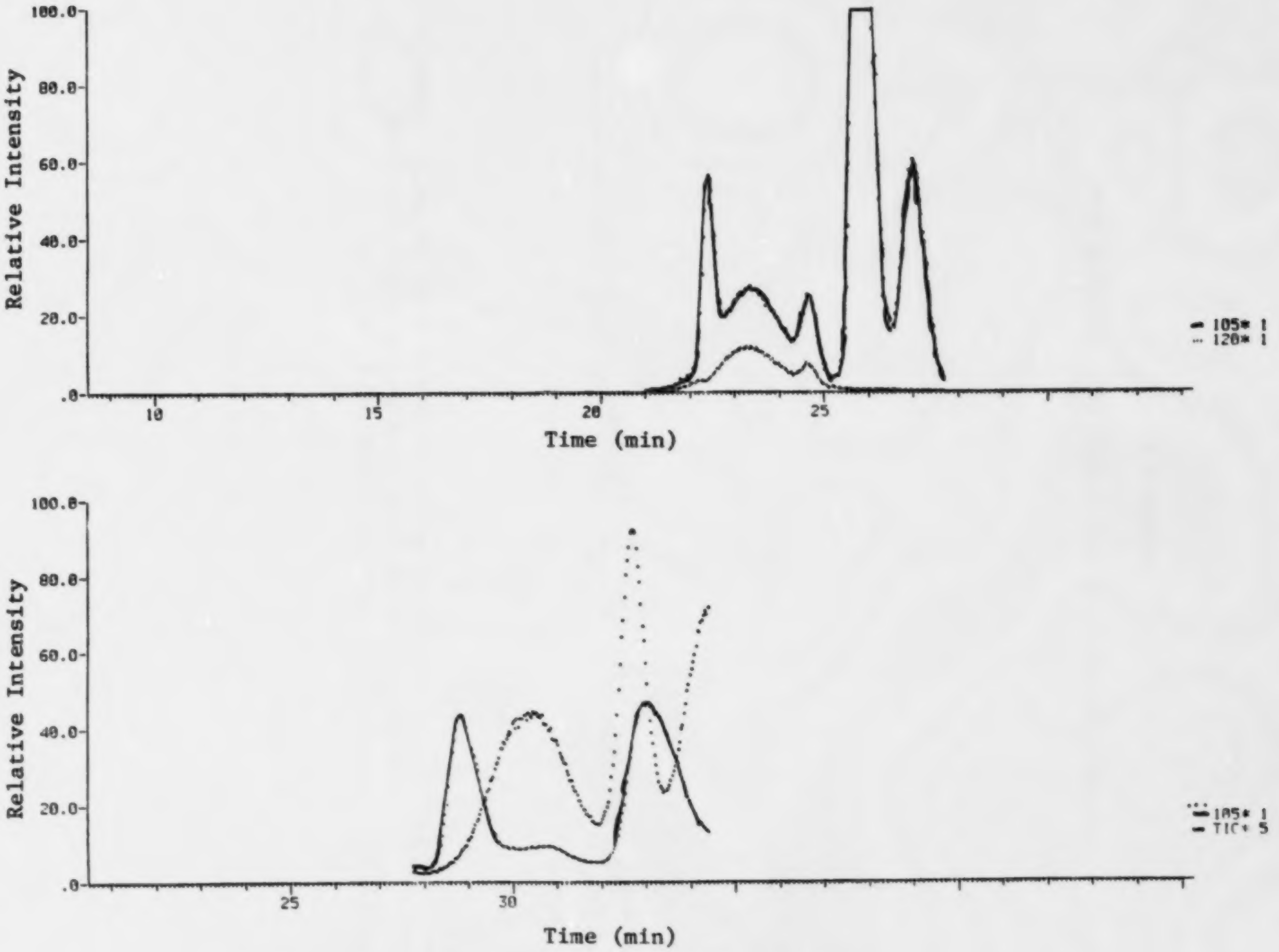


Figure A37. Mass chromatograms - m/z 105, 120.

APPENDIX B

VOLATILE ORGANICS IN AIR STREAM FROM AERATION POND

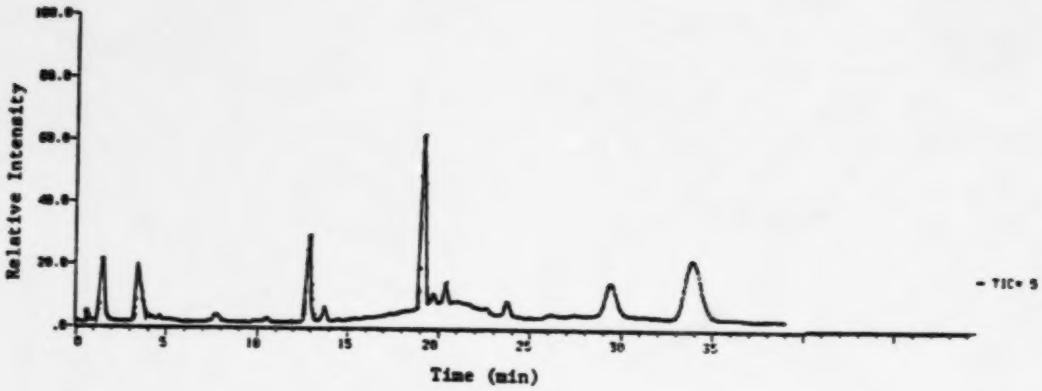


Figure B1. Reconstructed gc/ms chromatogram of volatile organics in air stream from aeration pond at S. Burlington, NC Treatment Plant (Sample 1, 1.0 ℓ).

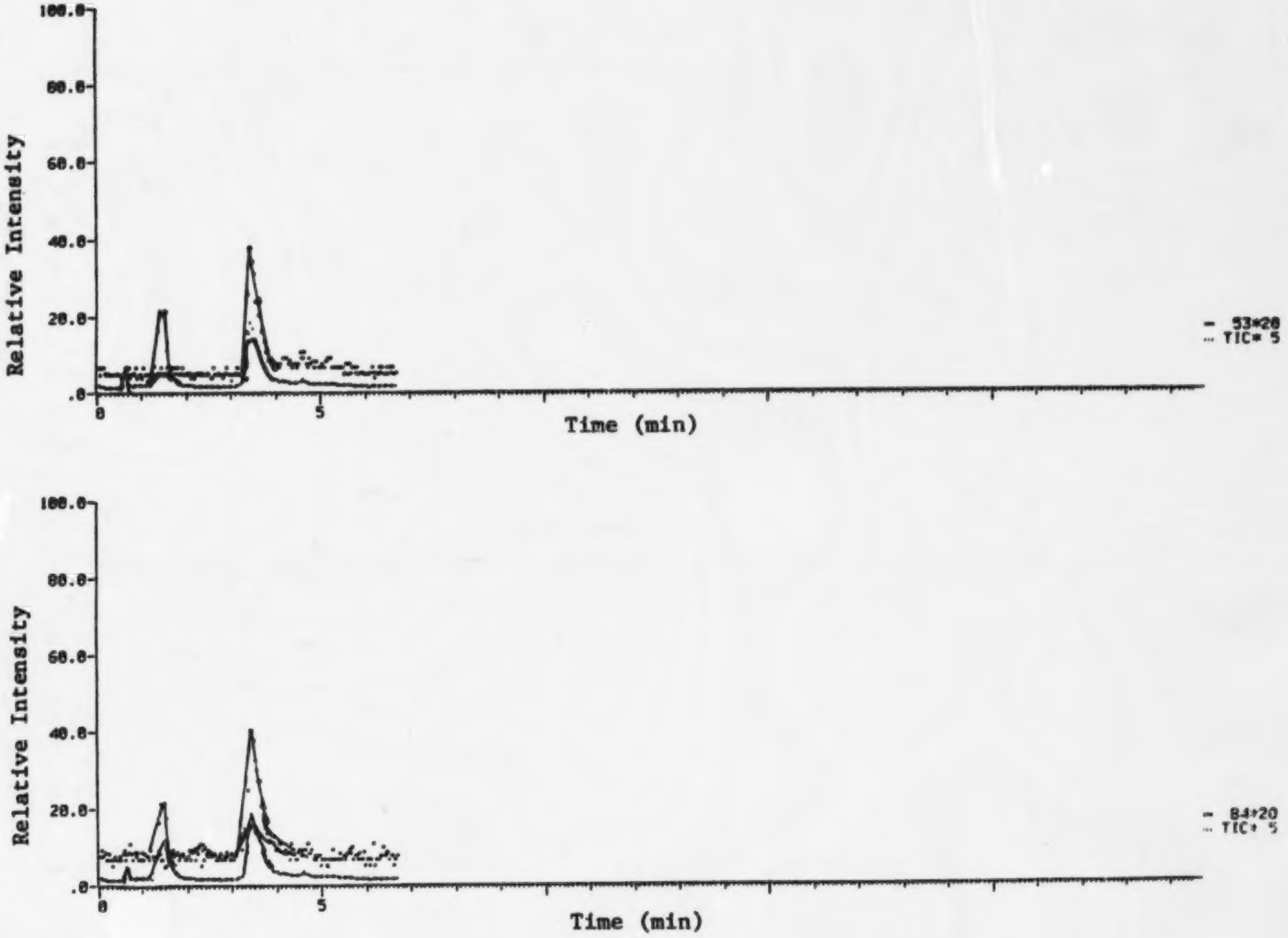


Figure B2. Mass chromatograms - m/z 53, 84.

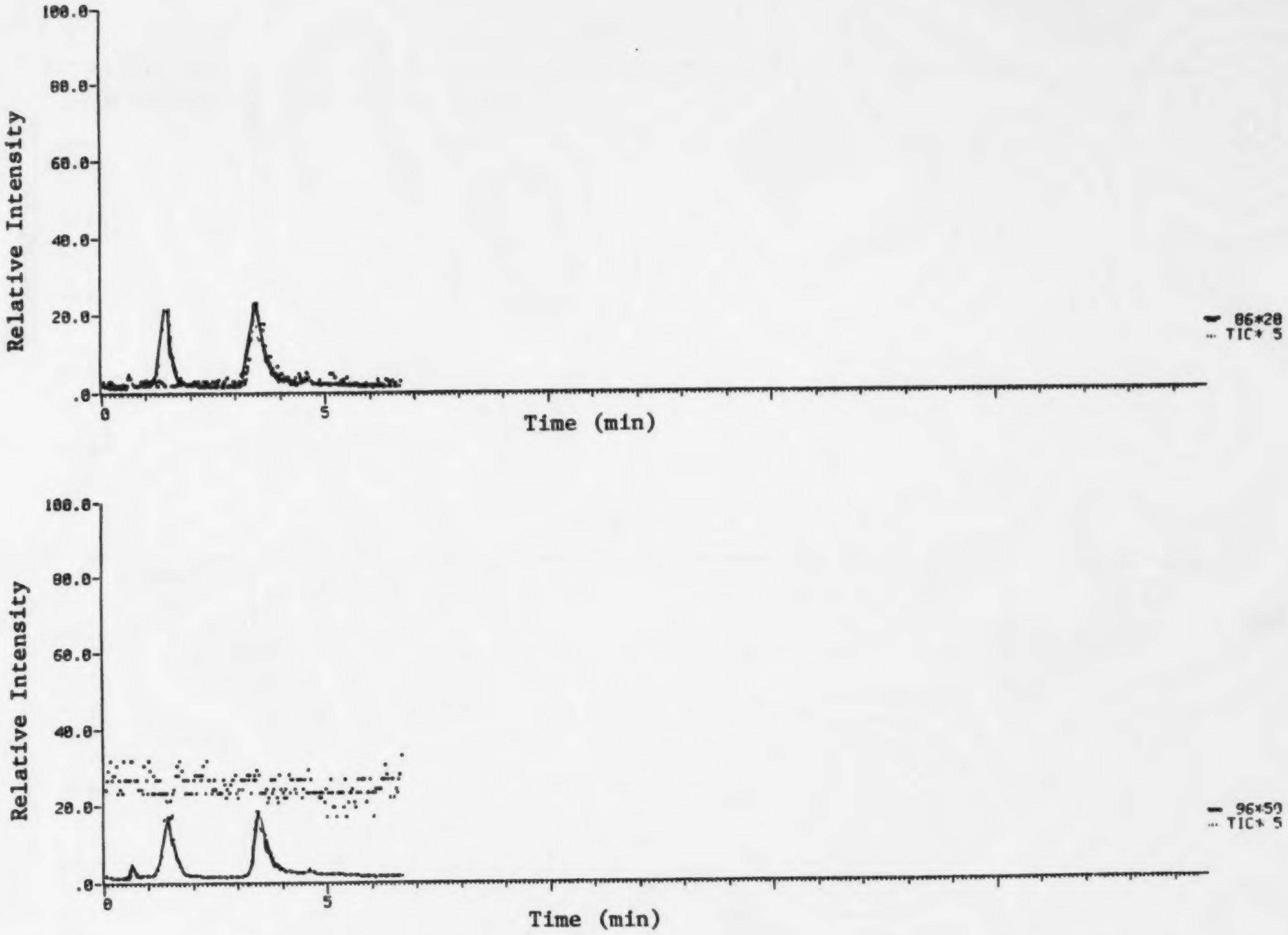


Figure B3. Mass chromatograms - m/z 86, 96.

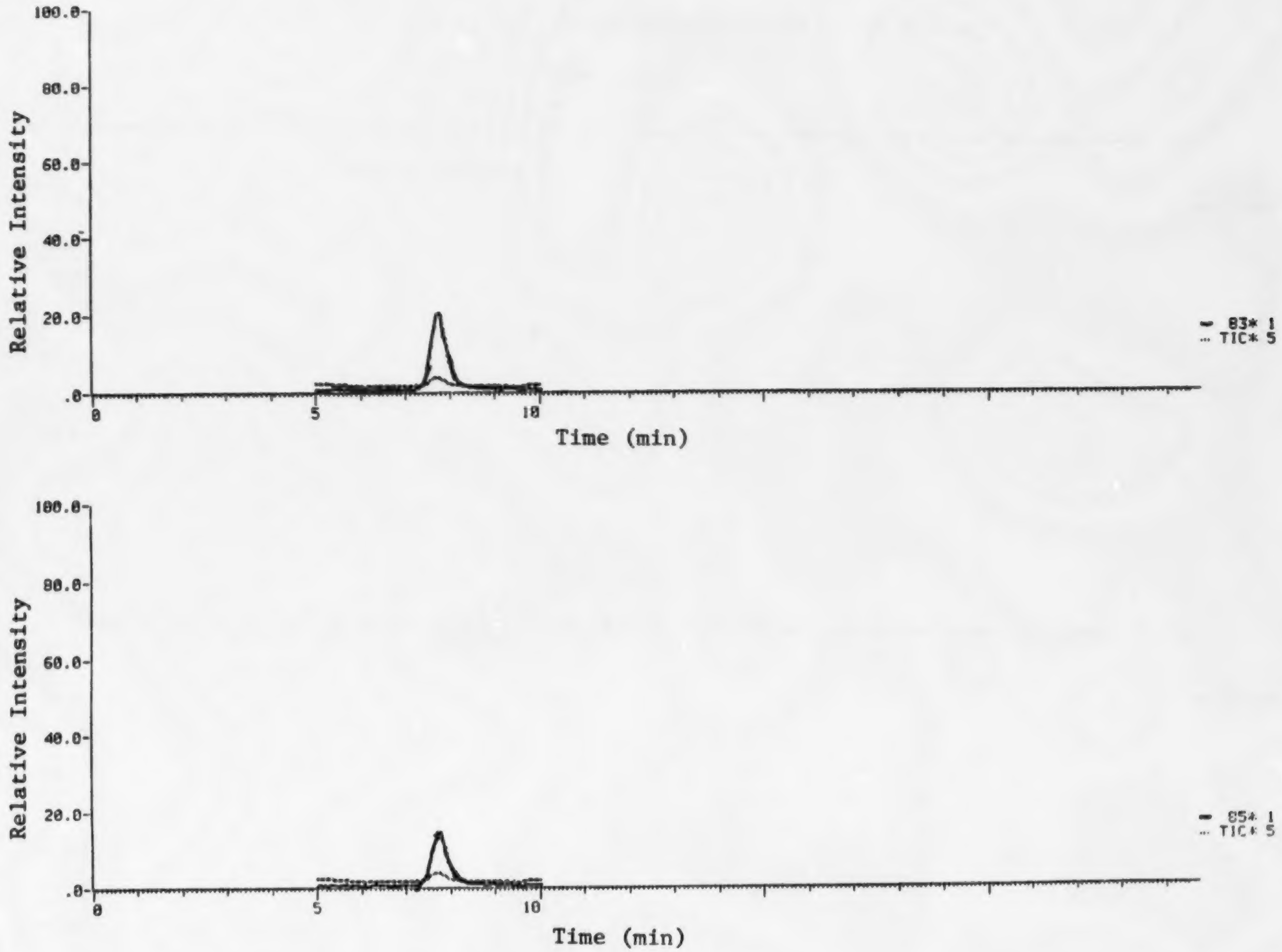


Figure B4. Mass chromatograms - m/z 83, 85.

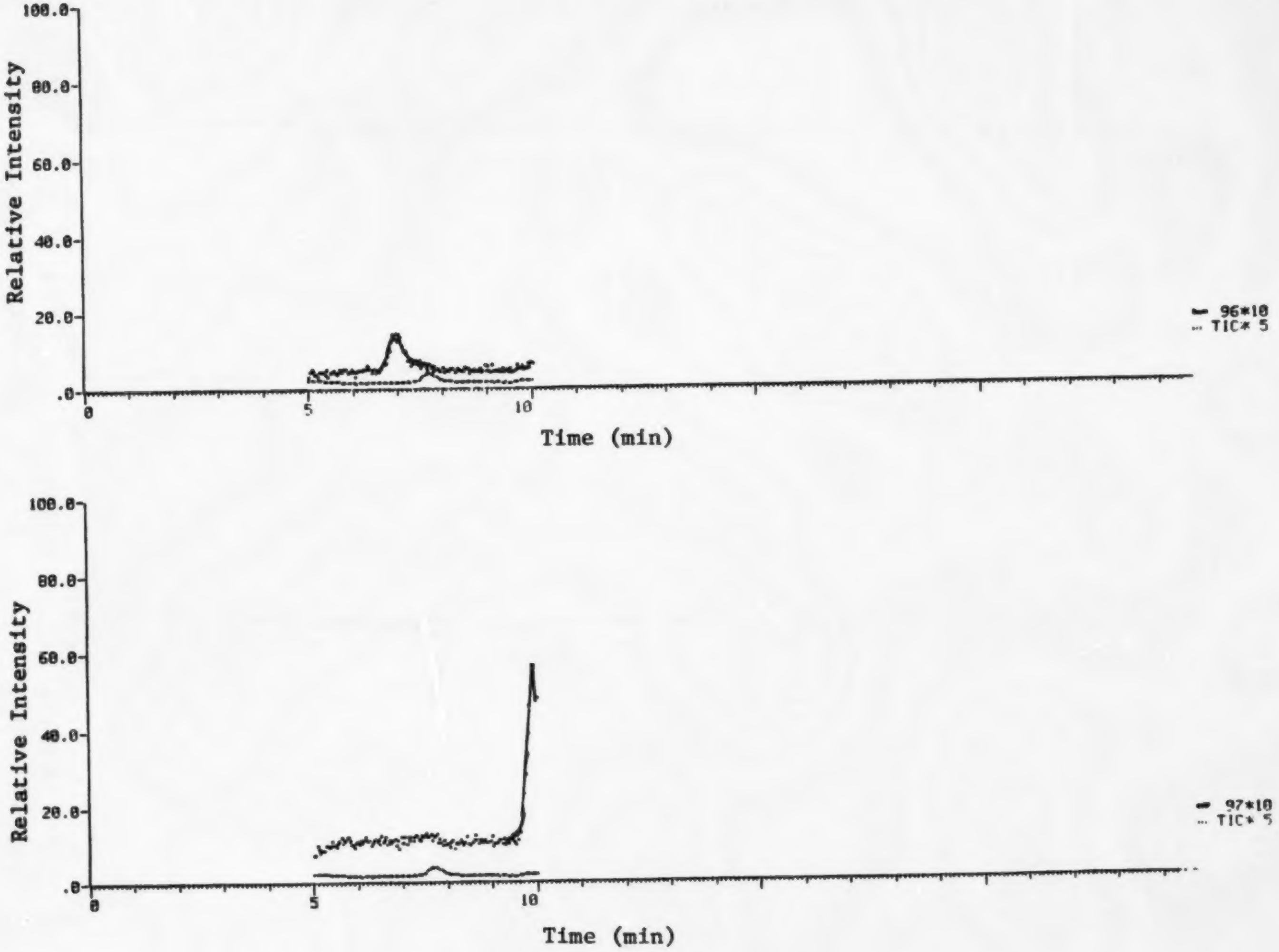


Figure B5. Mass chromatograms - m/z 96, 97.

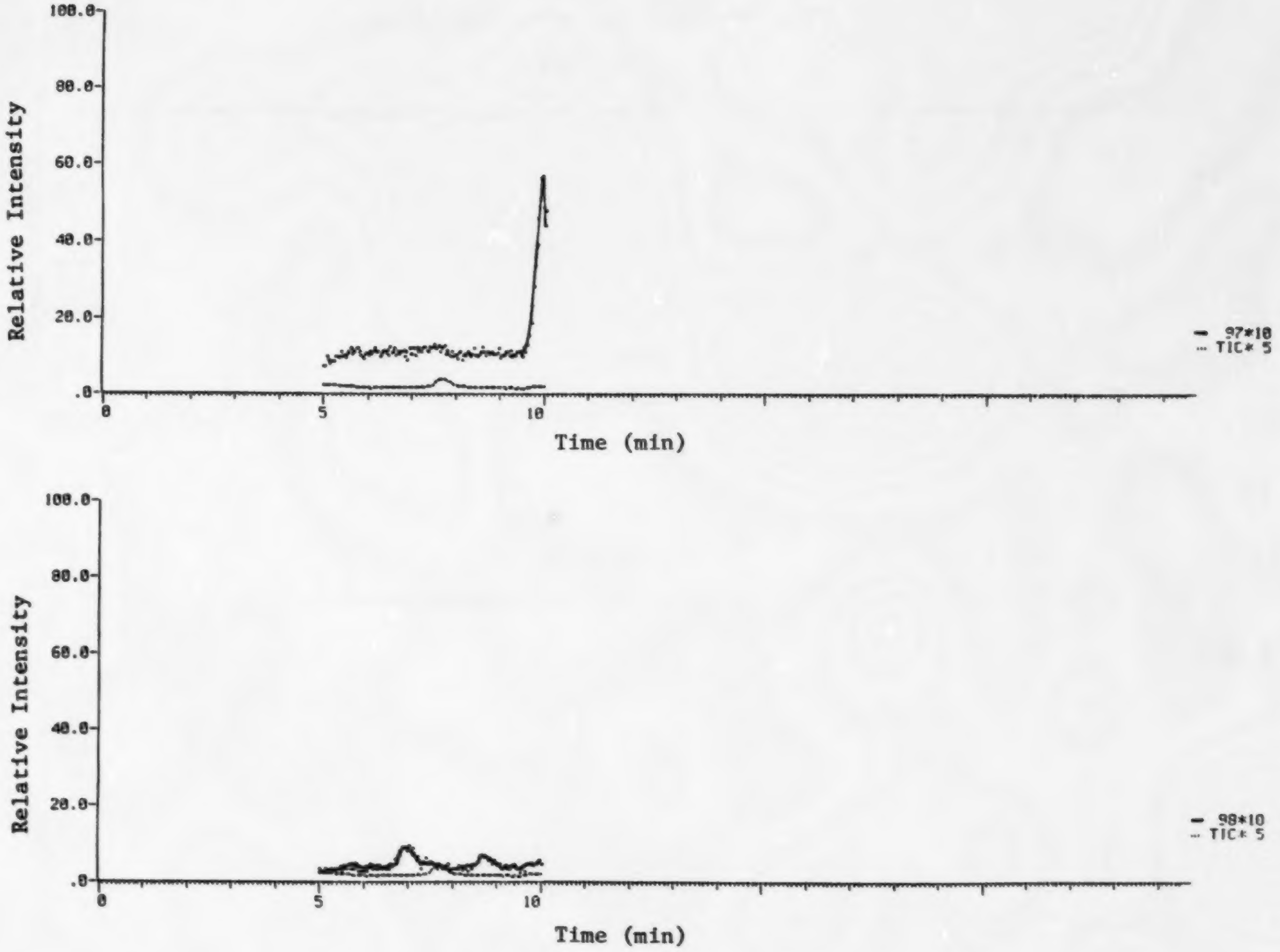


Figure B6. Mass chromatograms - m/z 97, 98.

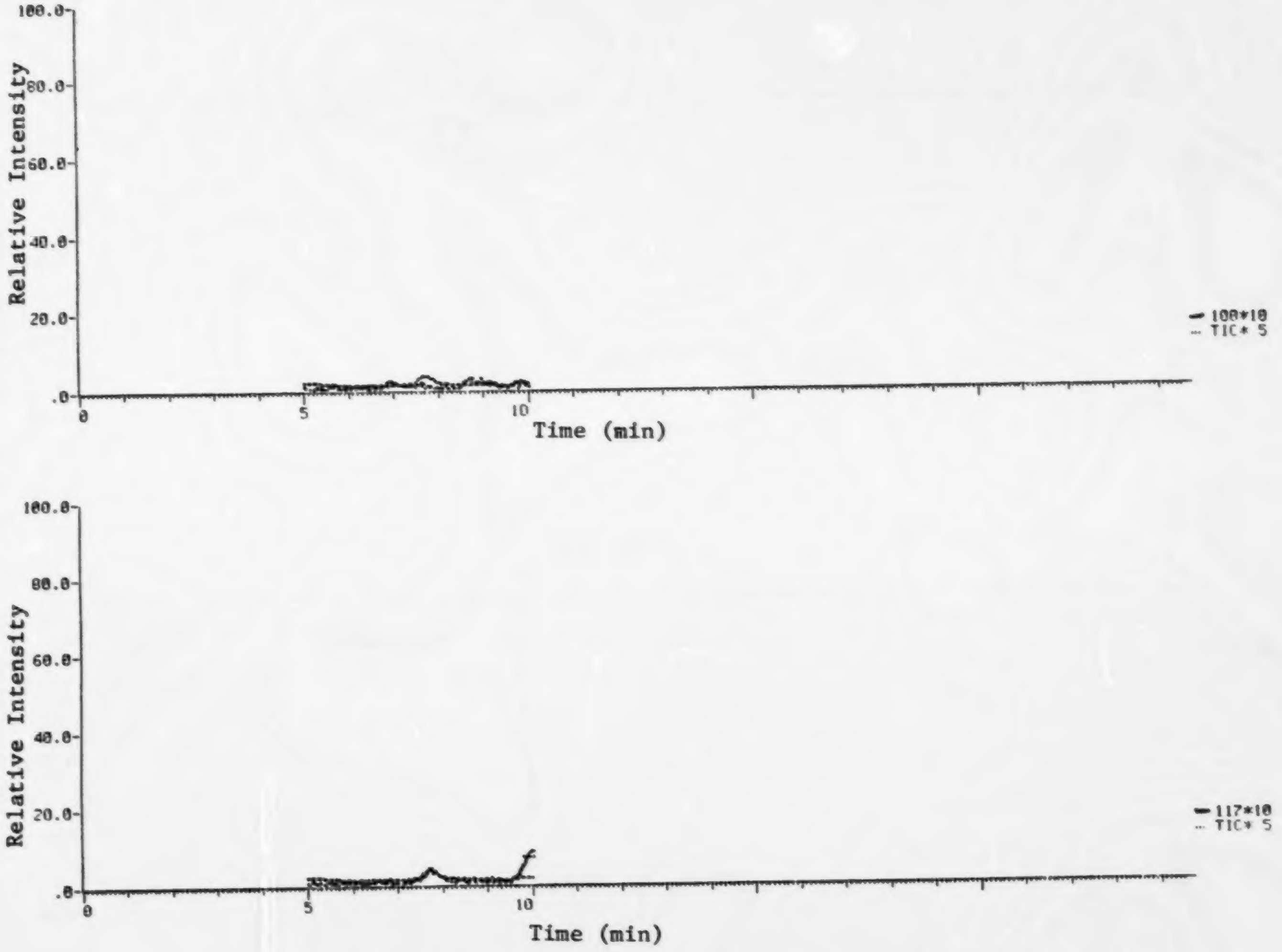


Figure B7. Mass chromatograms - m/z 100, 117.

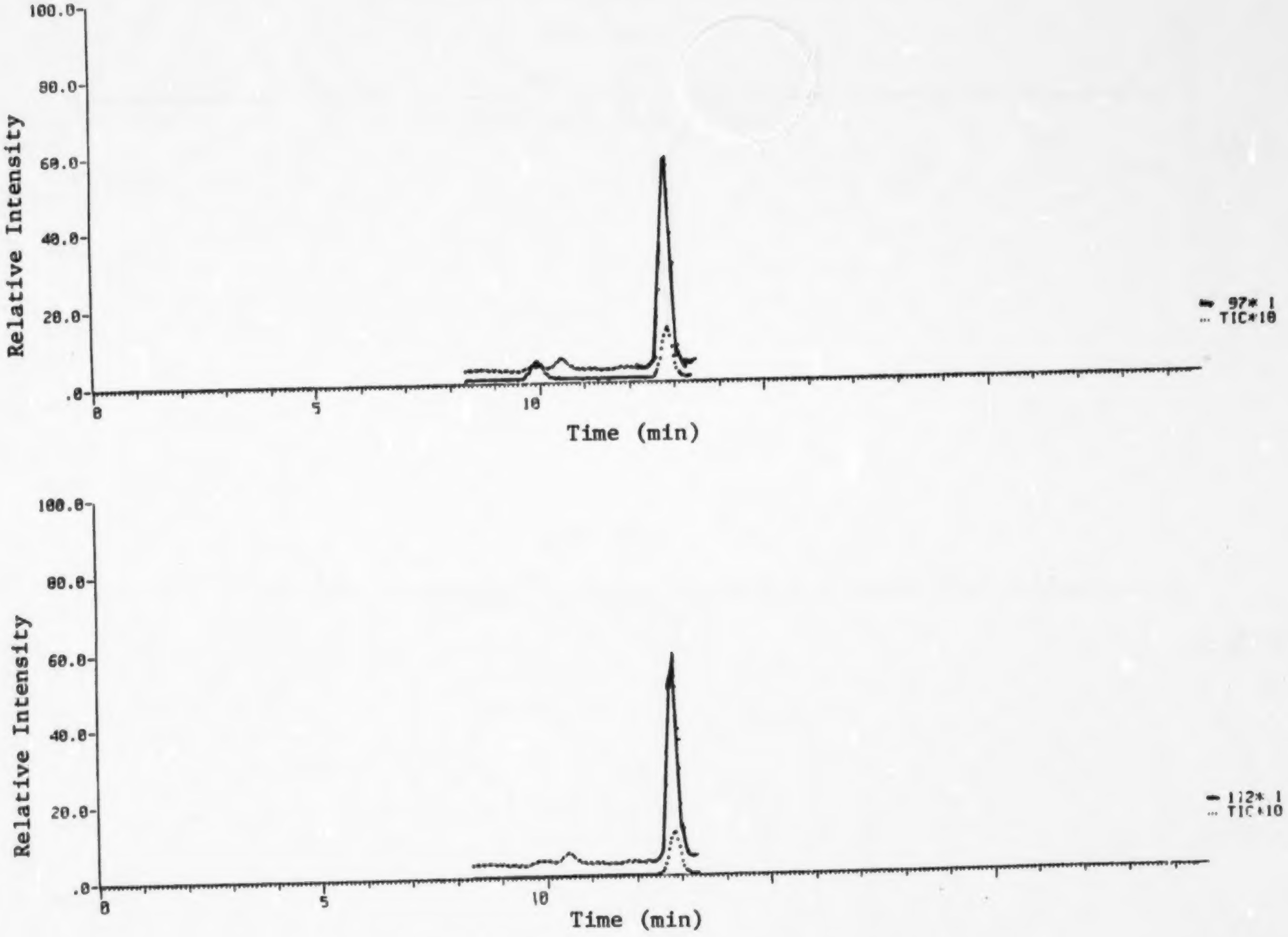


Figure B8. Mass chromatograms - m/z 97, 112.

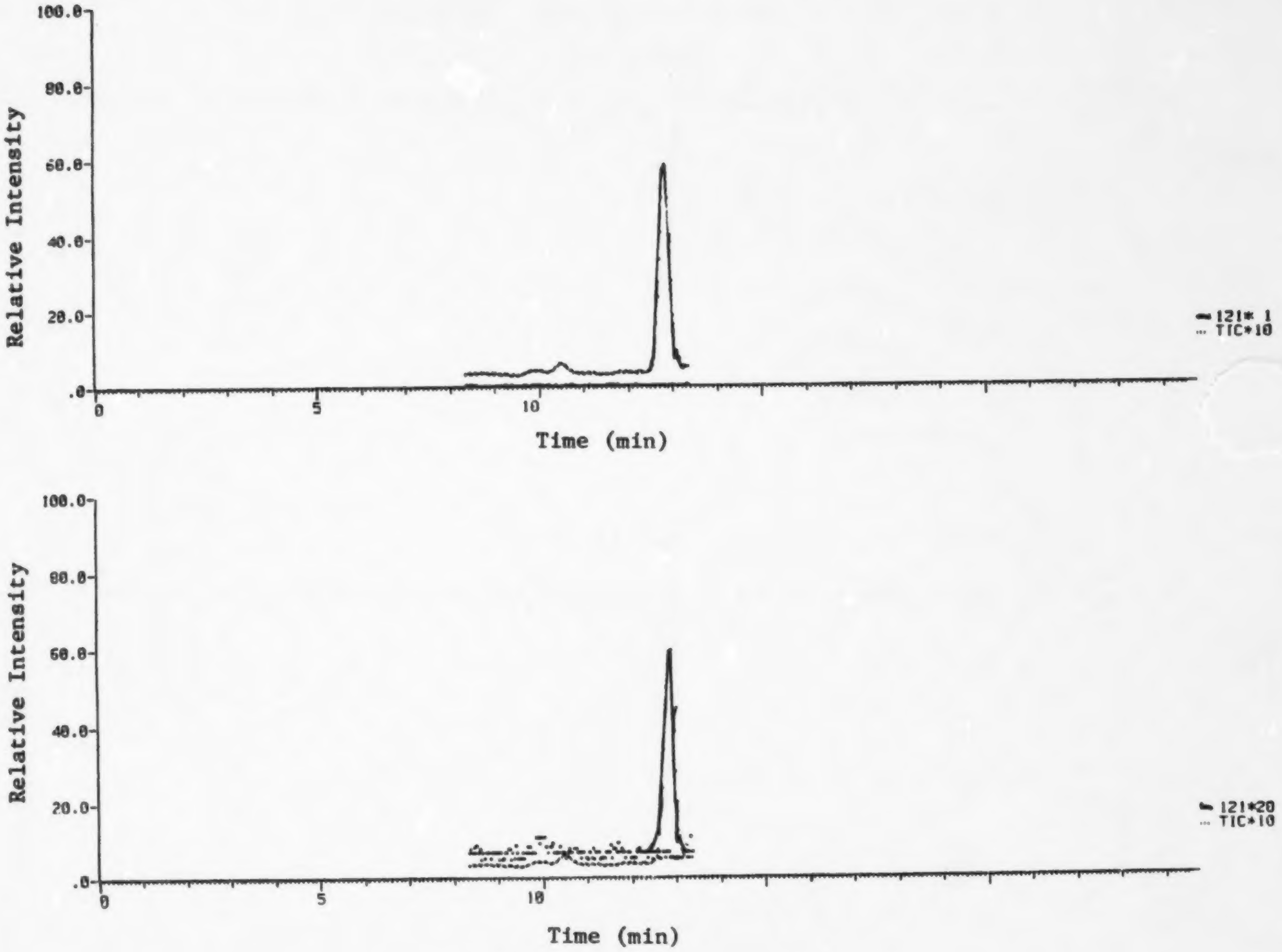


Figure B9. Mass chromatograms - m/z 121.

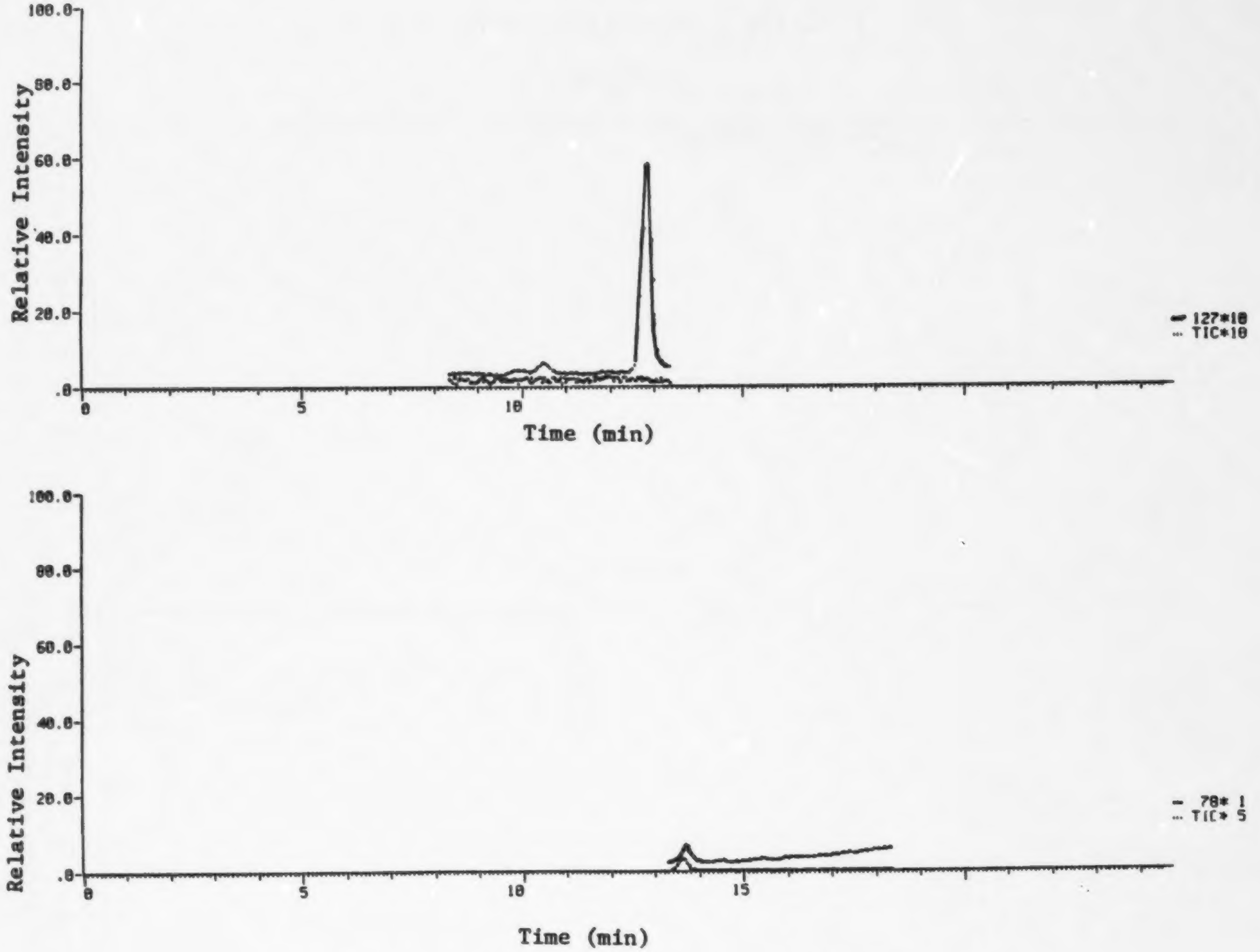


Figure B10. Mass chromatograms - 127, 78.

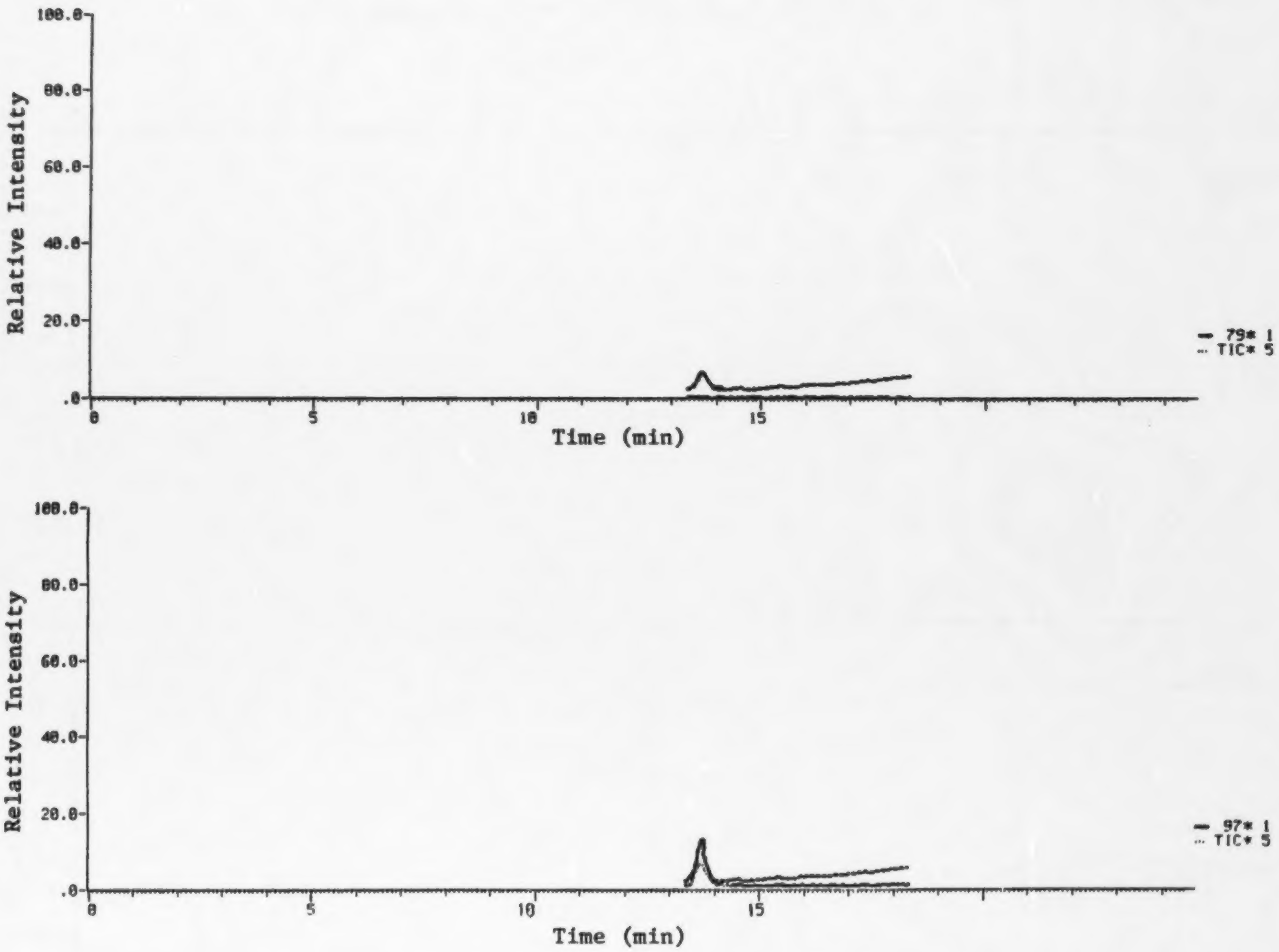


Figure B11. Mass chromatograms - m/z 79, 97.

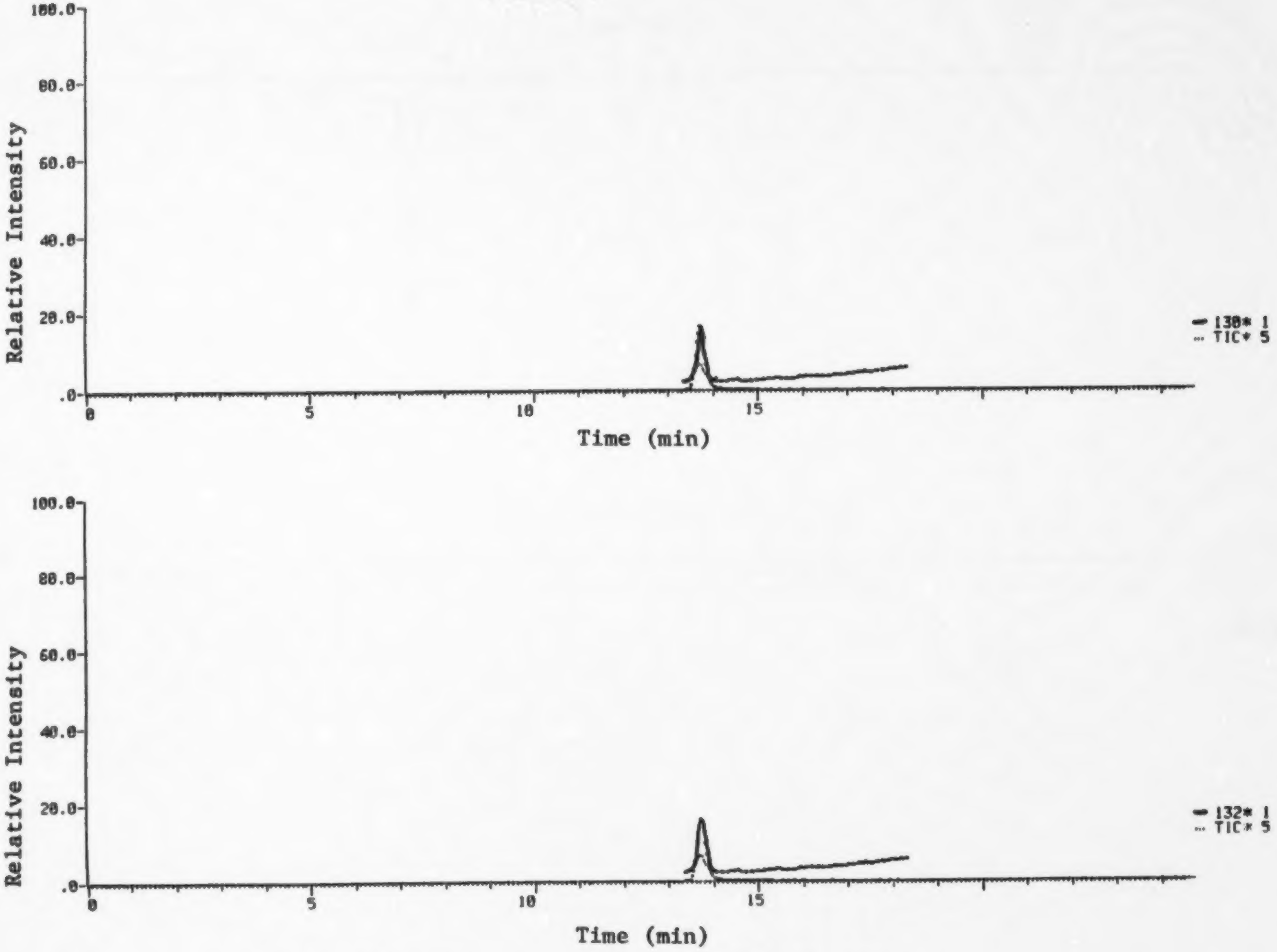


Figure B12. Mass chromatograms - m/z 130, 132.

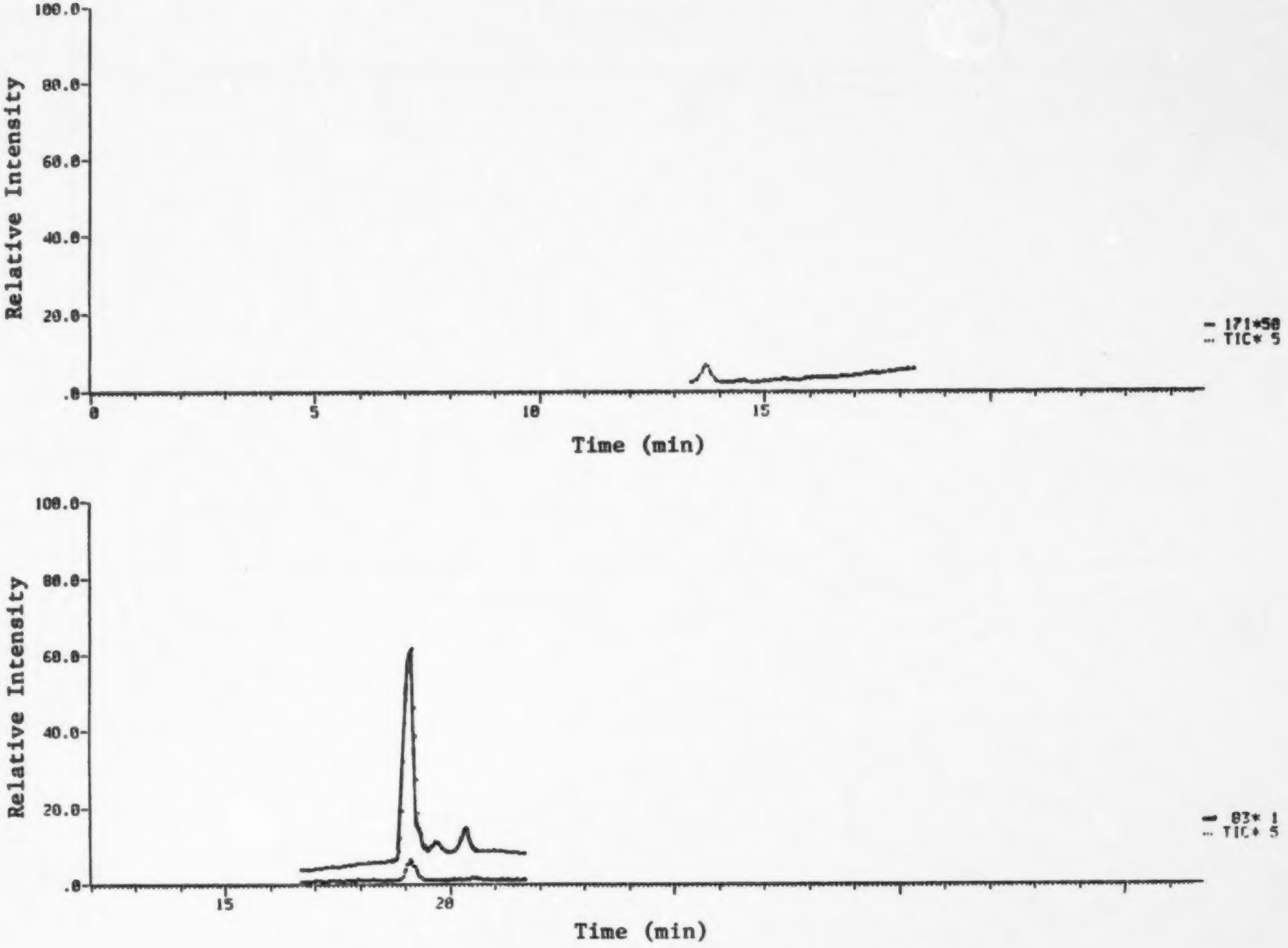


Figure B13. Mass chromatograms - m/z 171, 83.

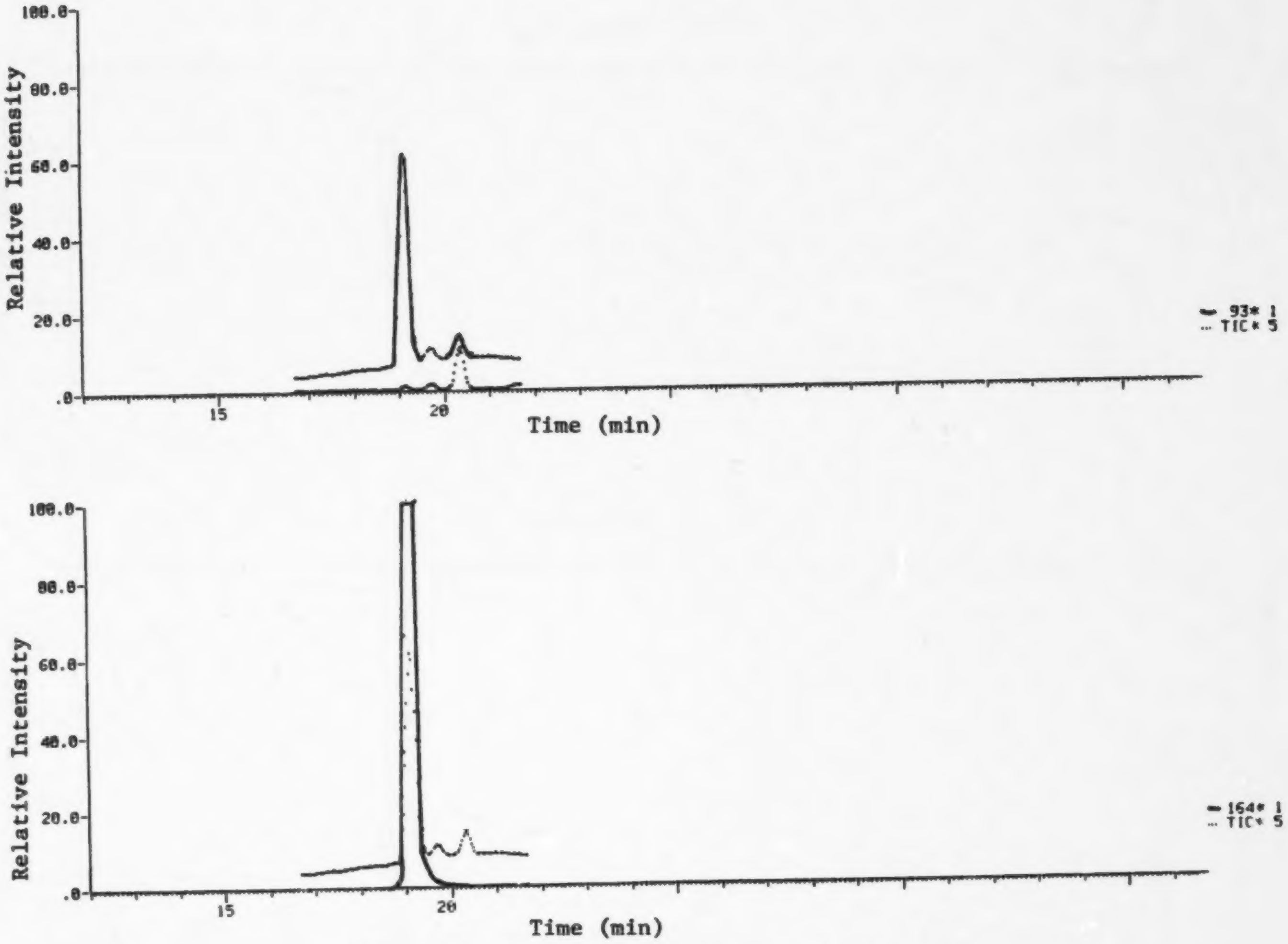


Figure B14. Mass chromatograms - m/z 93, 164.

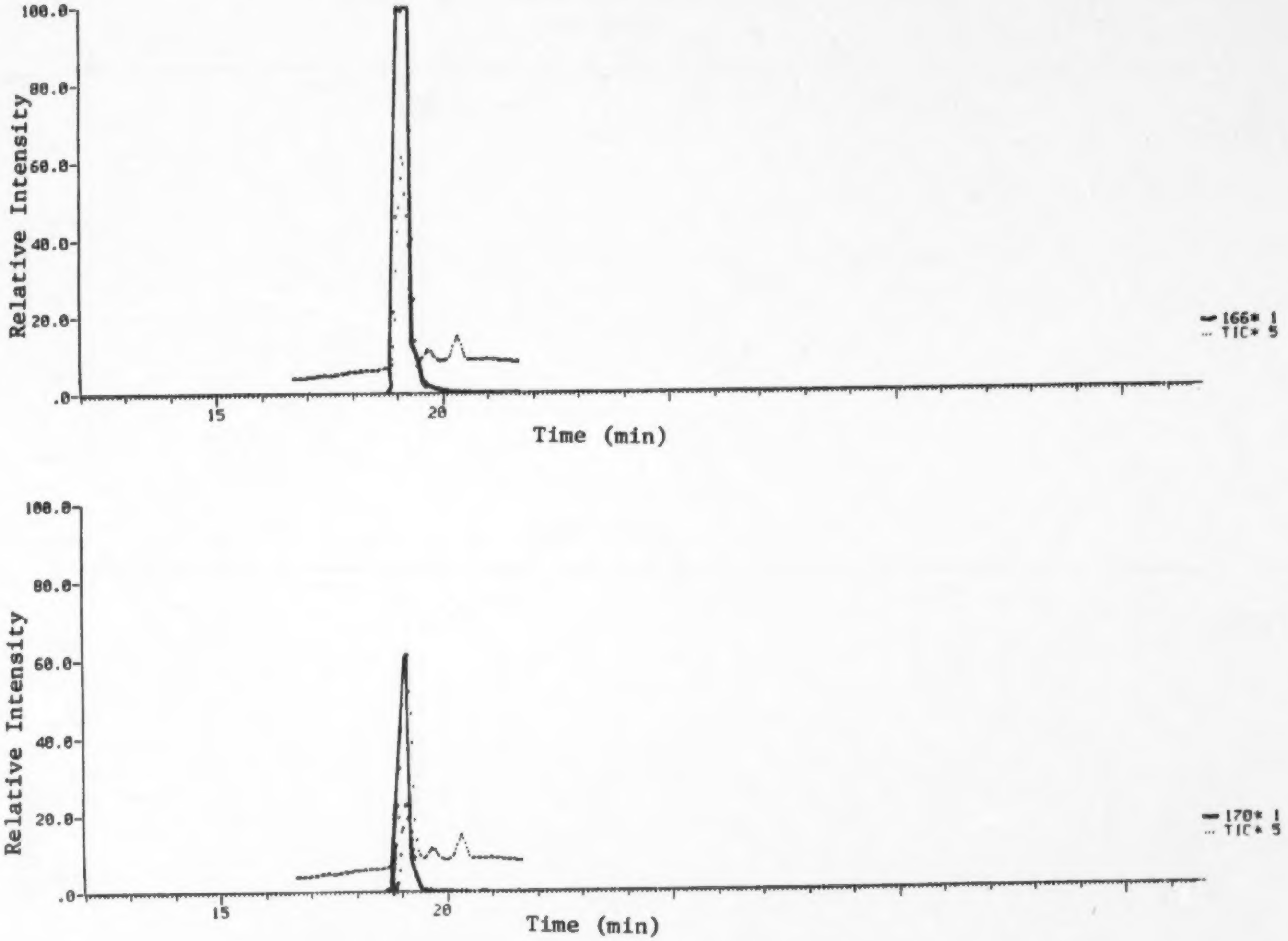


Figure B15. Mass chromatograms - m/z 166, 170.

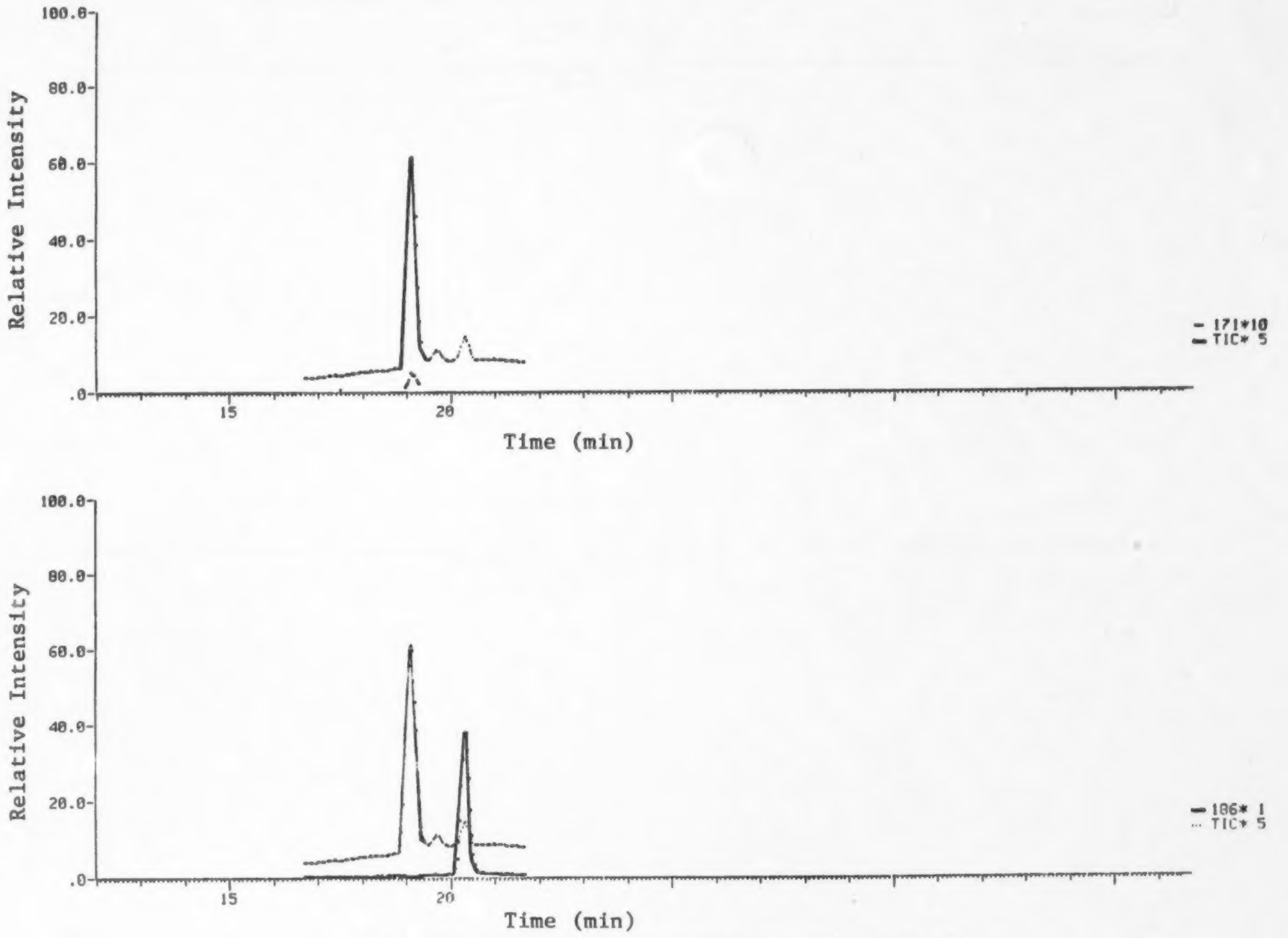


Figure B16. Mass chromatograms - m/z 171, 186.

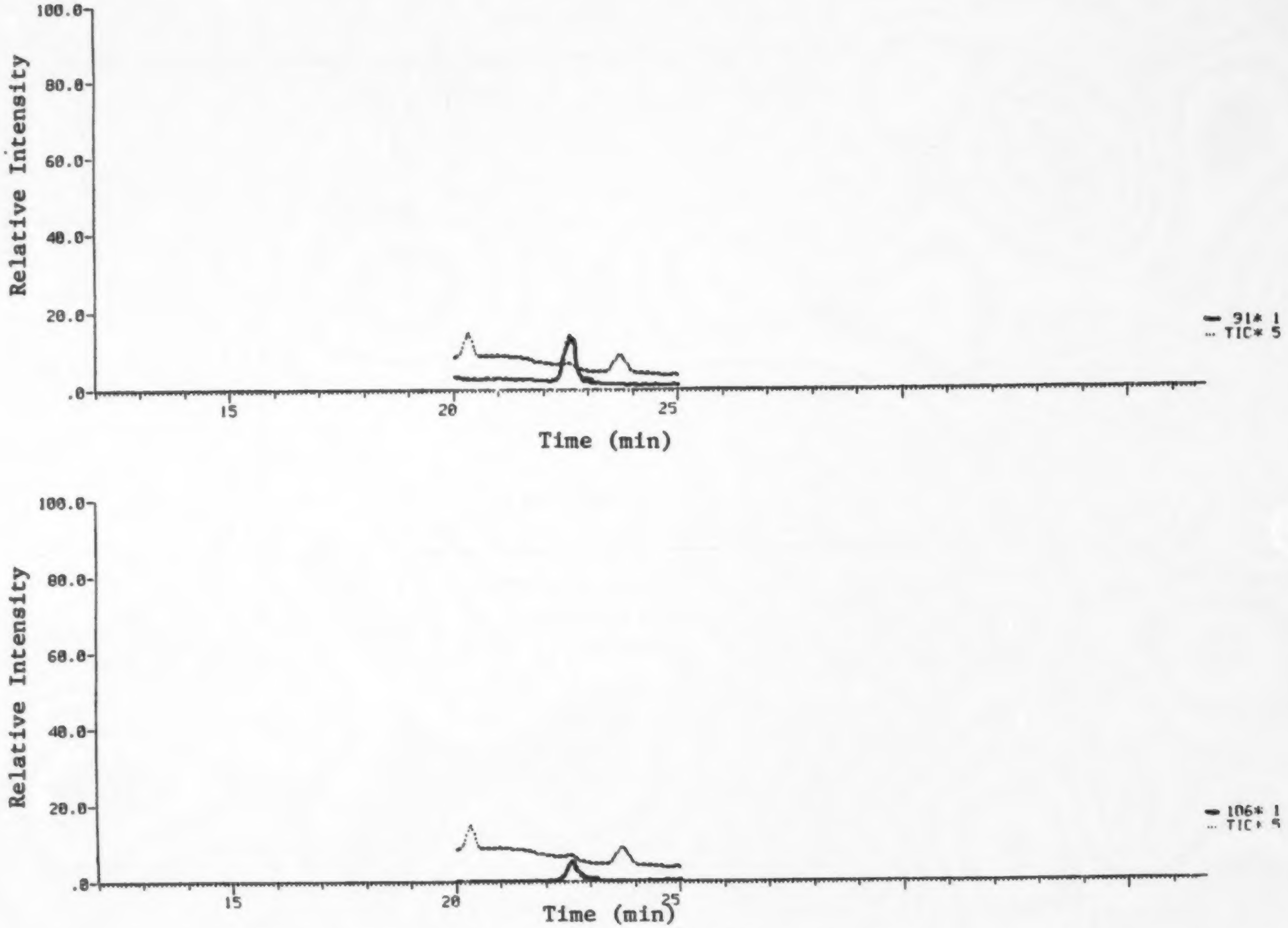


Figure B17. Mass chromatograms - m/z 91, 106.

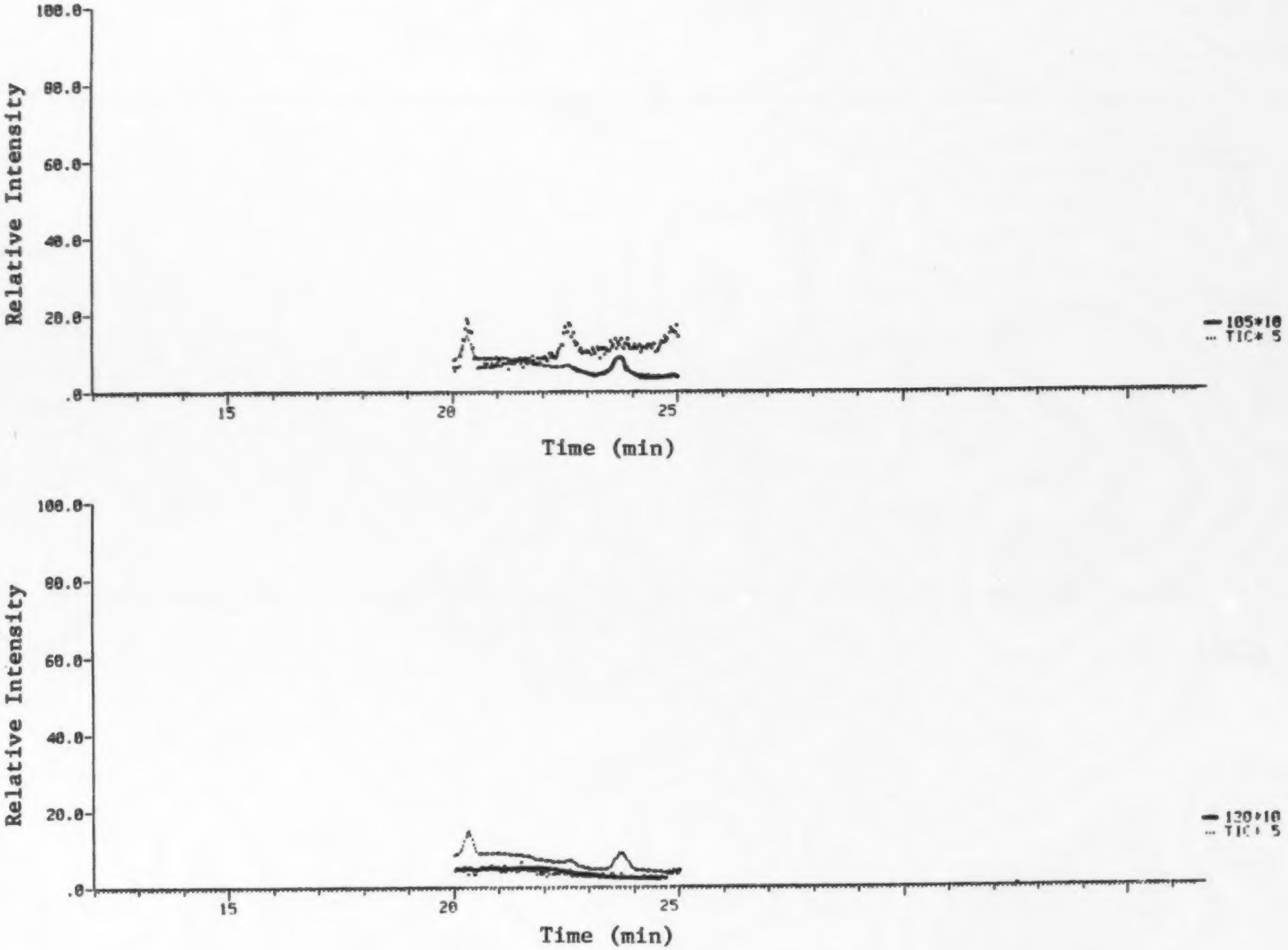


Figure B18. Mass chromatograms - m/z 105, 120.

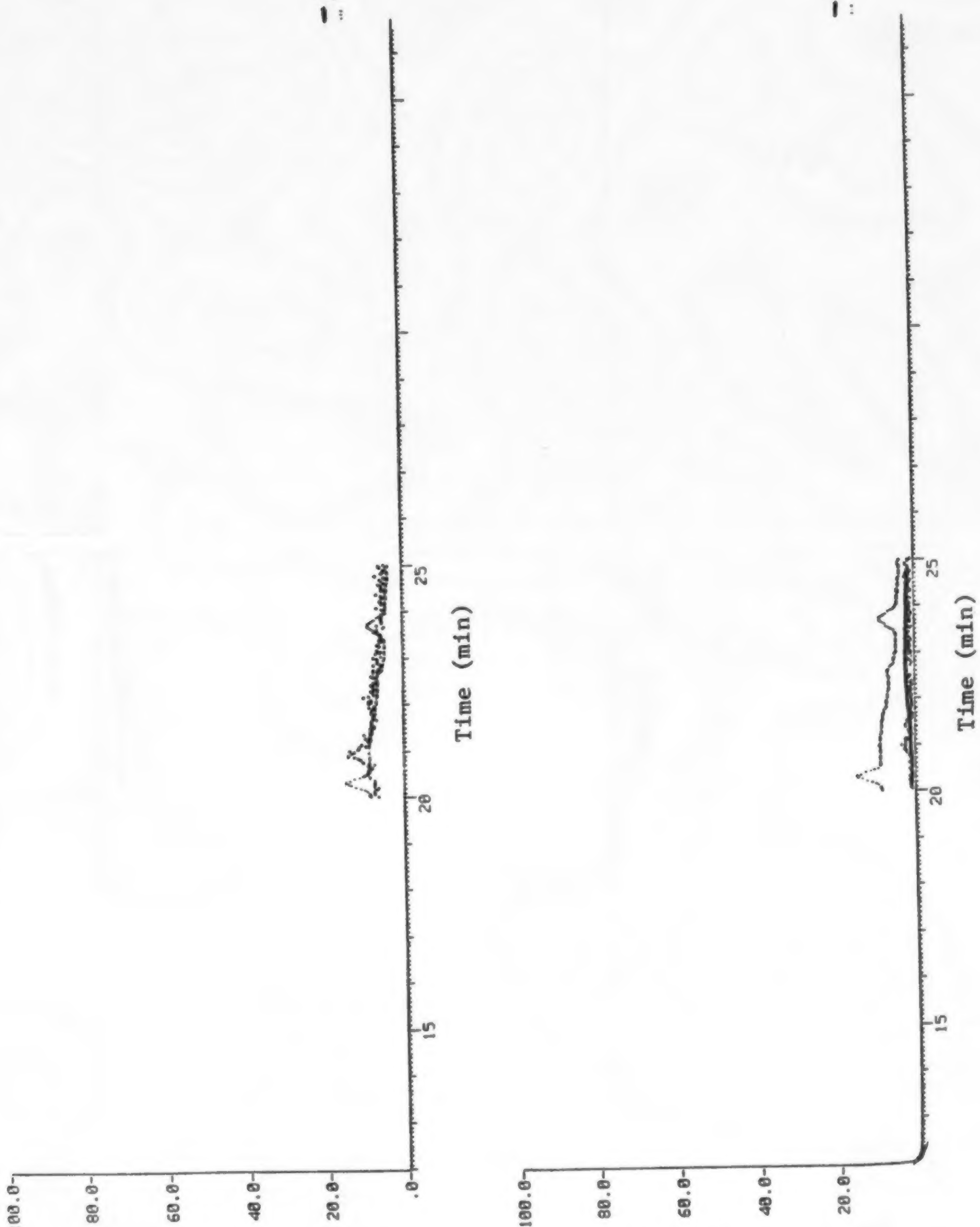


Figure B19. Mass chromatograms - m/z 112, 114.

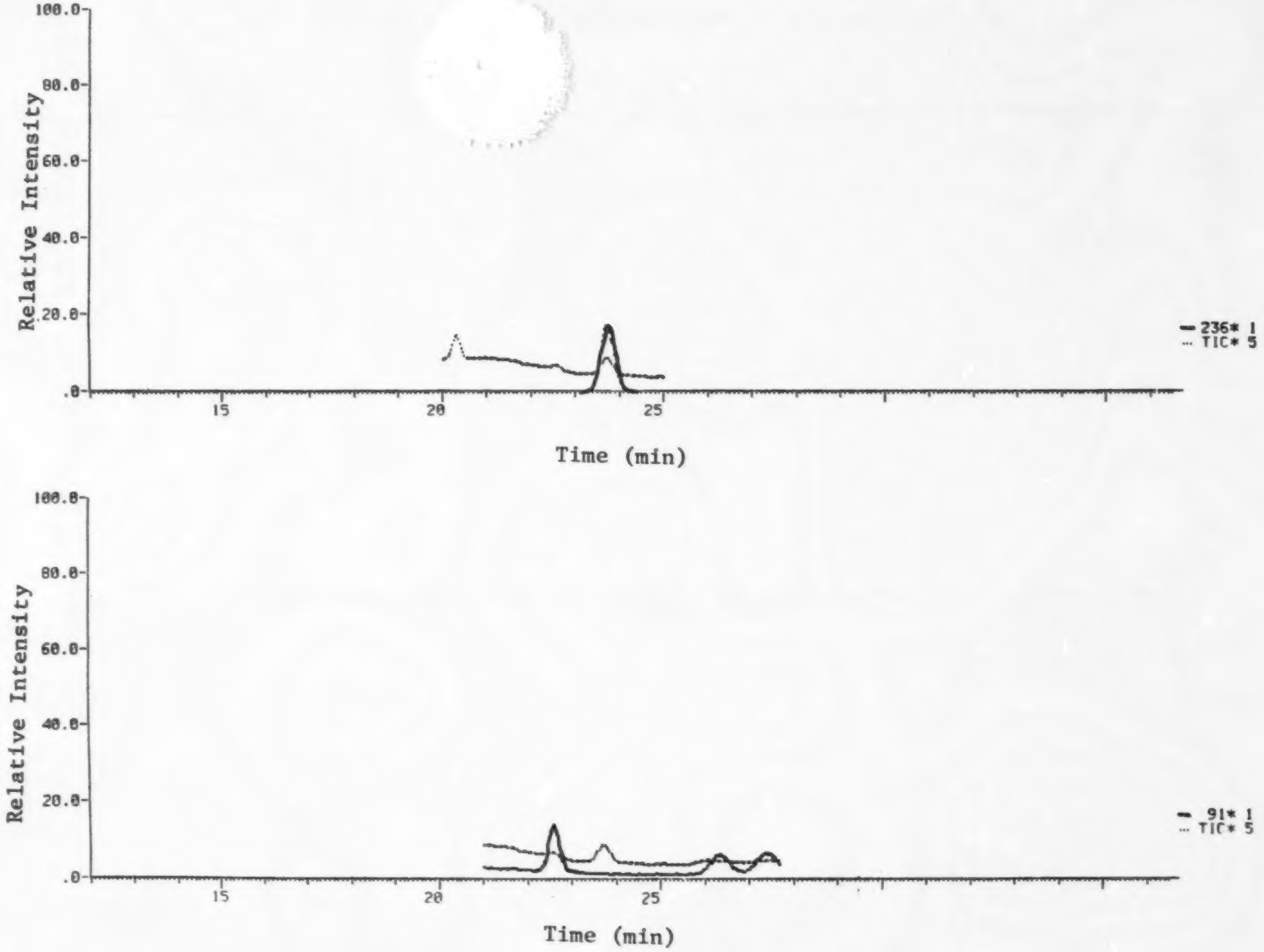


Figure B20. Mass chromatograms - m/z 236, 91.

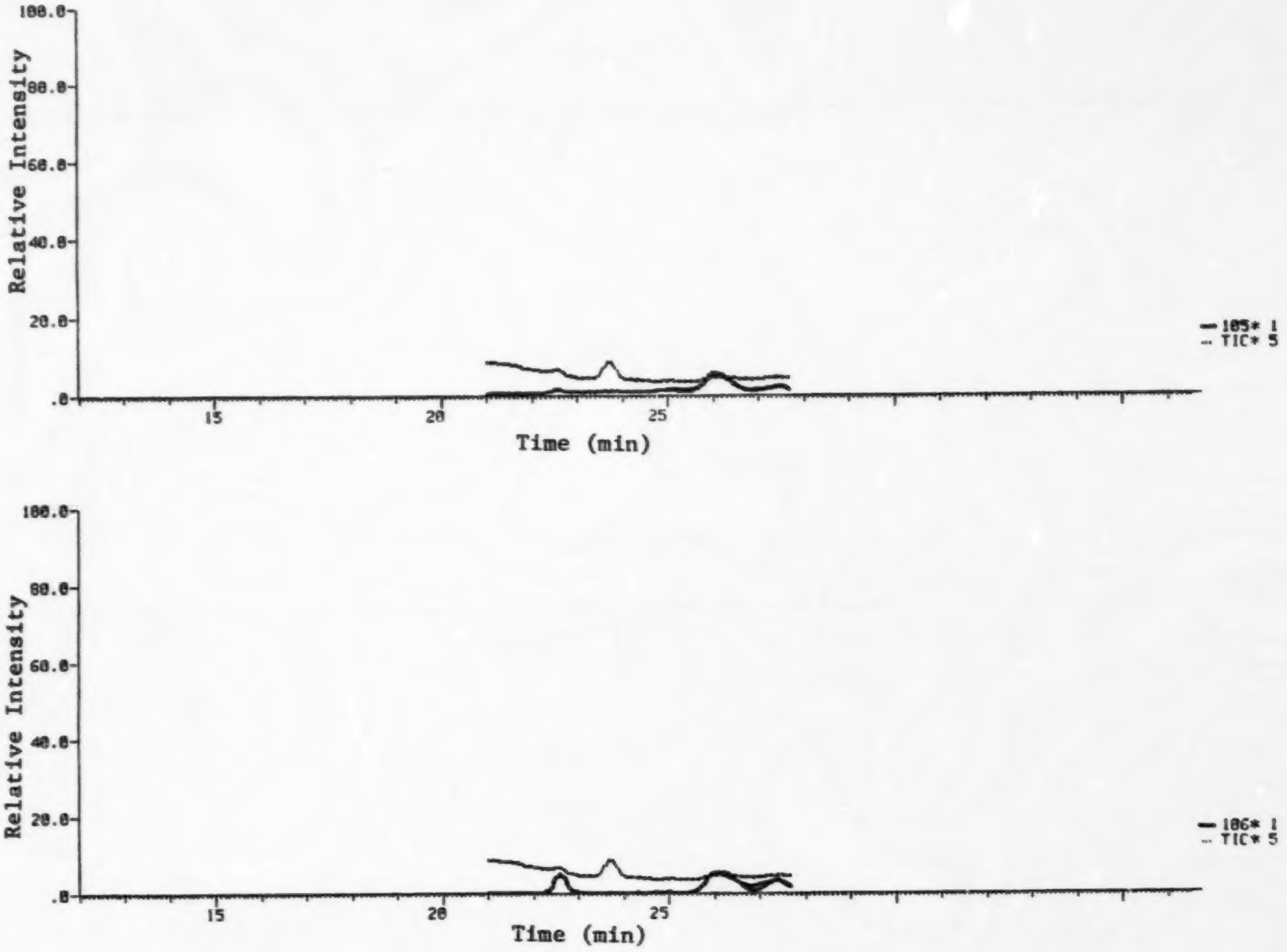


Figure B21. Mass chromatograms - m/z 105, 106.

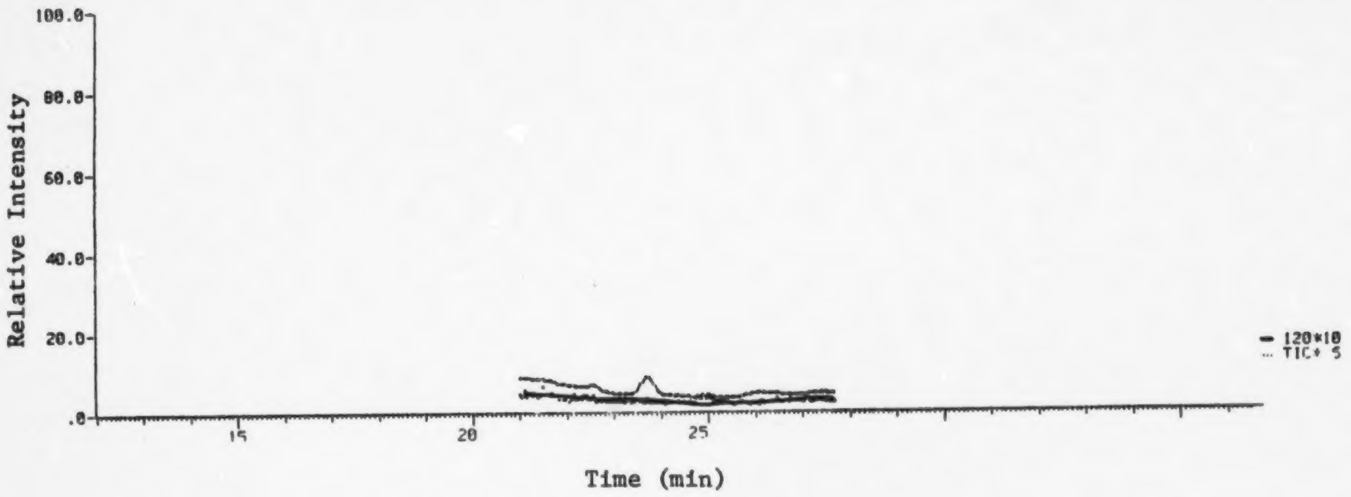


Figure B22. Mass chromatogram - m/z 120.

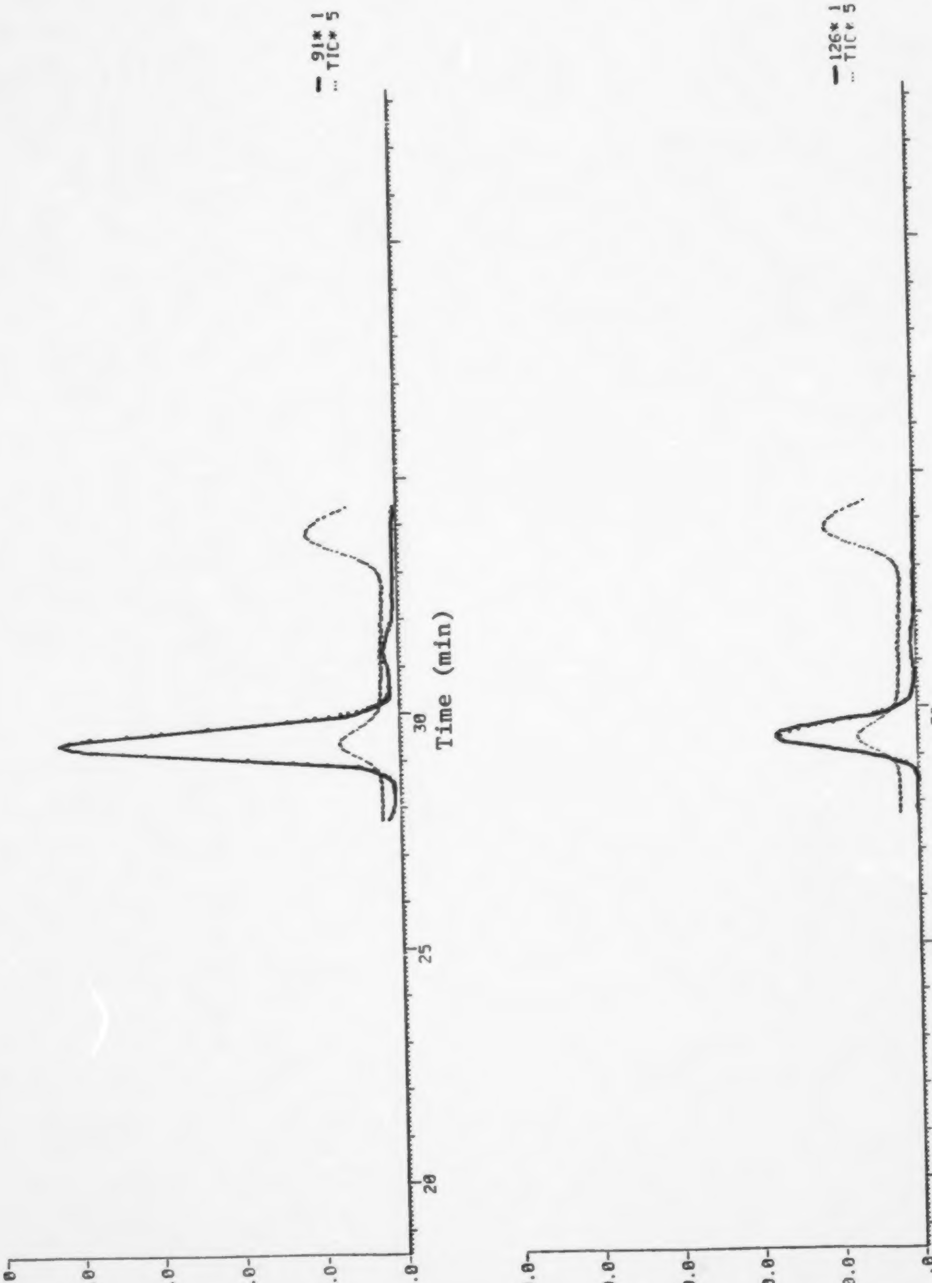


Figure B23. Mass chromatograms - m/z 91, 126.

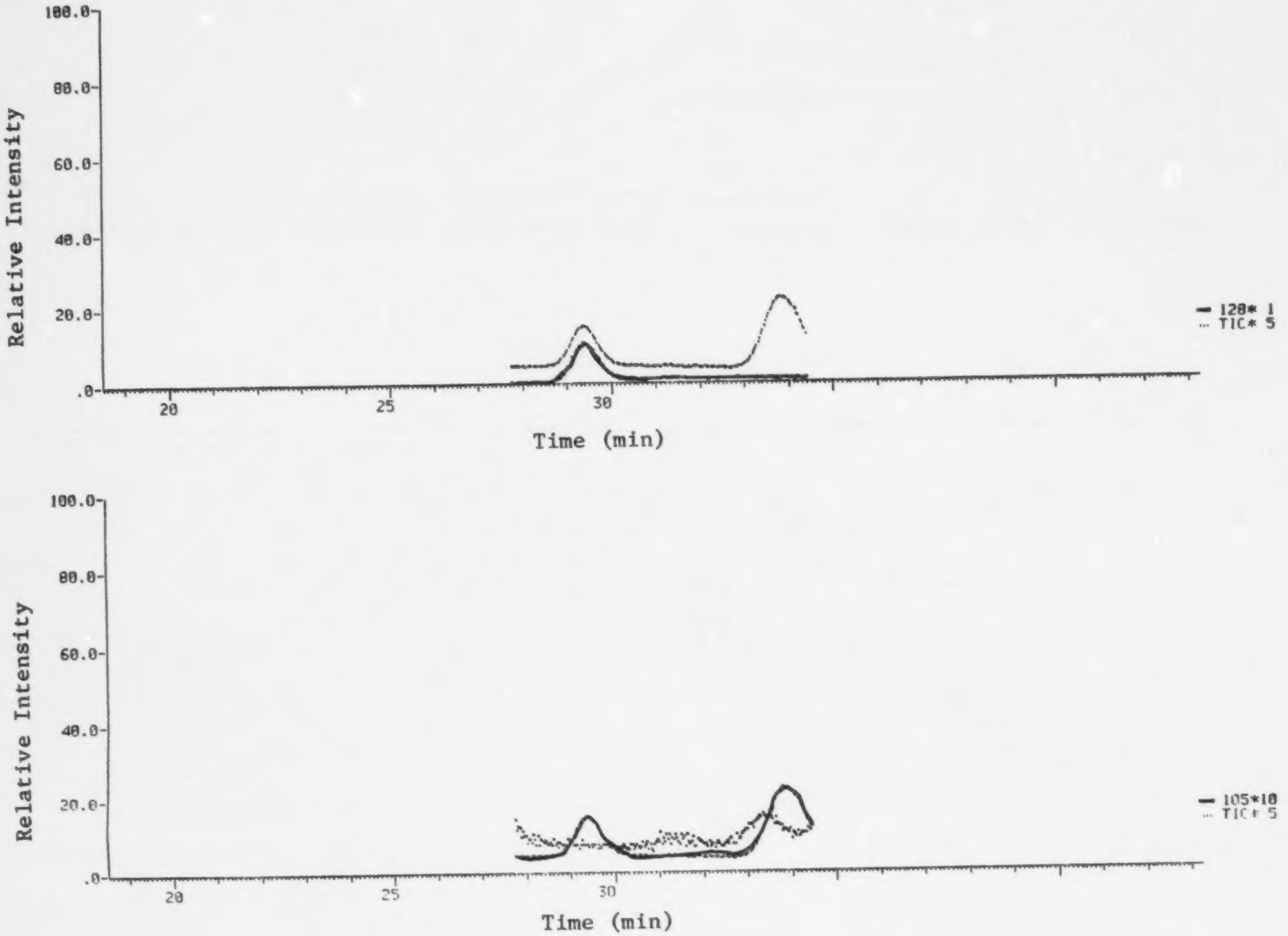


Figure B24. Mass chromatograms - m/z 128, 105.

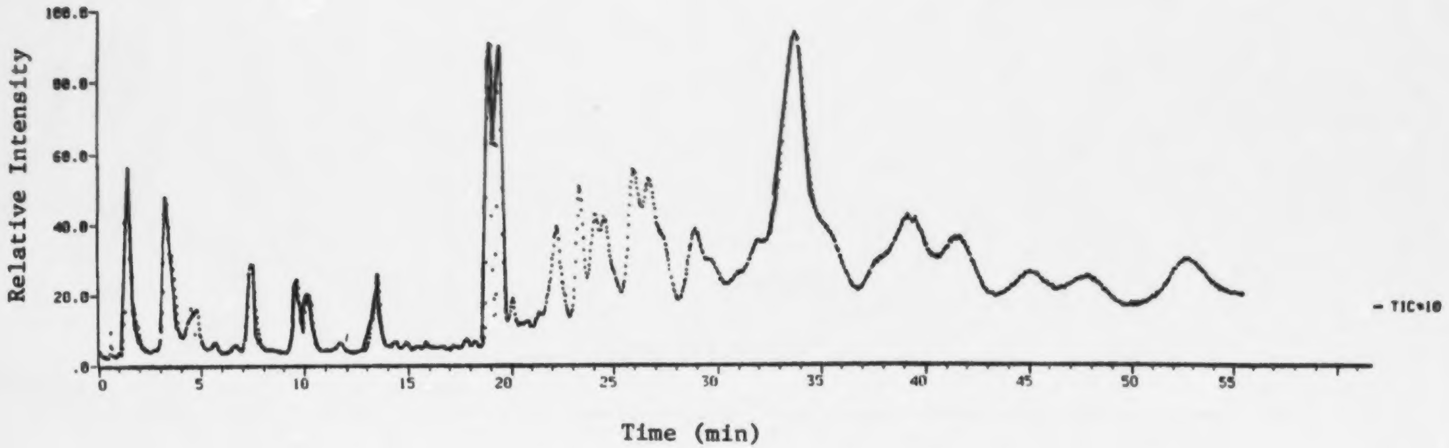


Figure B25. Reconstructed GC/MS chromatogram of volatile organics in air stream from aeration basin at Durham, NC treatment plant.

APPENDIX C

VOLATILE ORGANICS IN VENT FROM PURE OXYGEN (CLOSED CHAMBER) SYSTEM

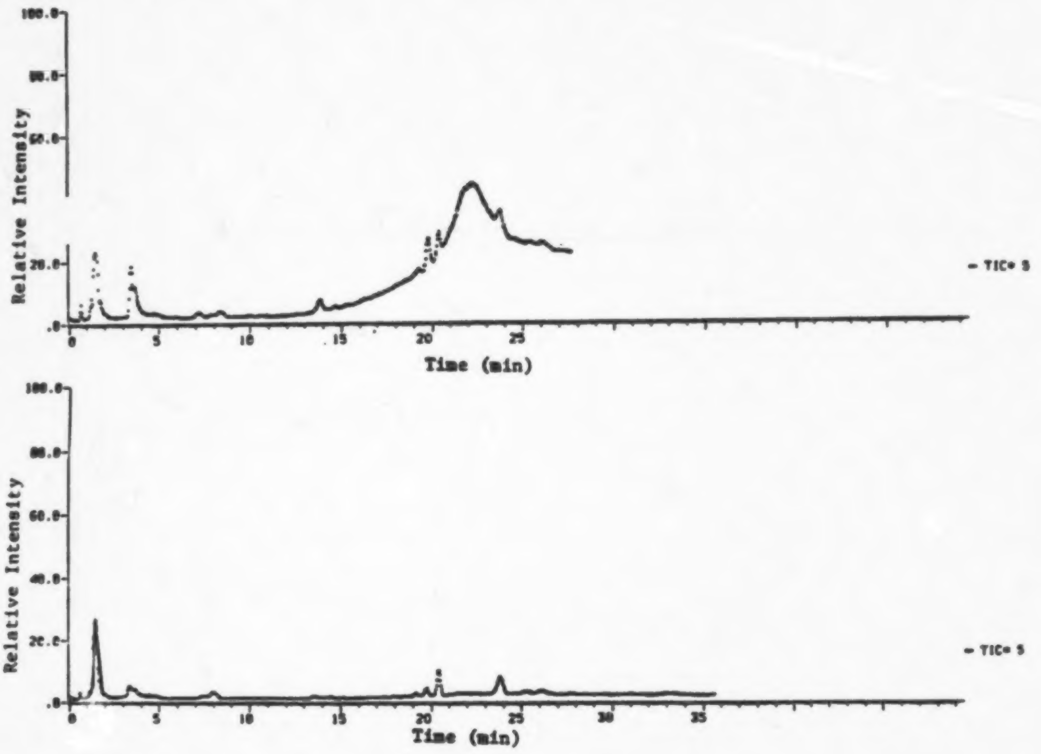


Figure C1. Reconstructed GC/MS chromatograms for volatile organics in vent of closed chamber at Danville, VA Treatment Plant.

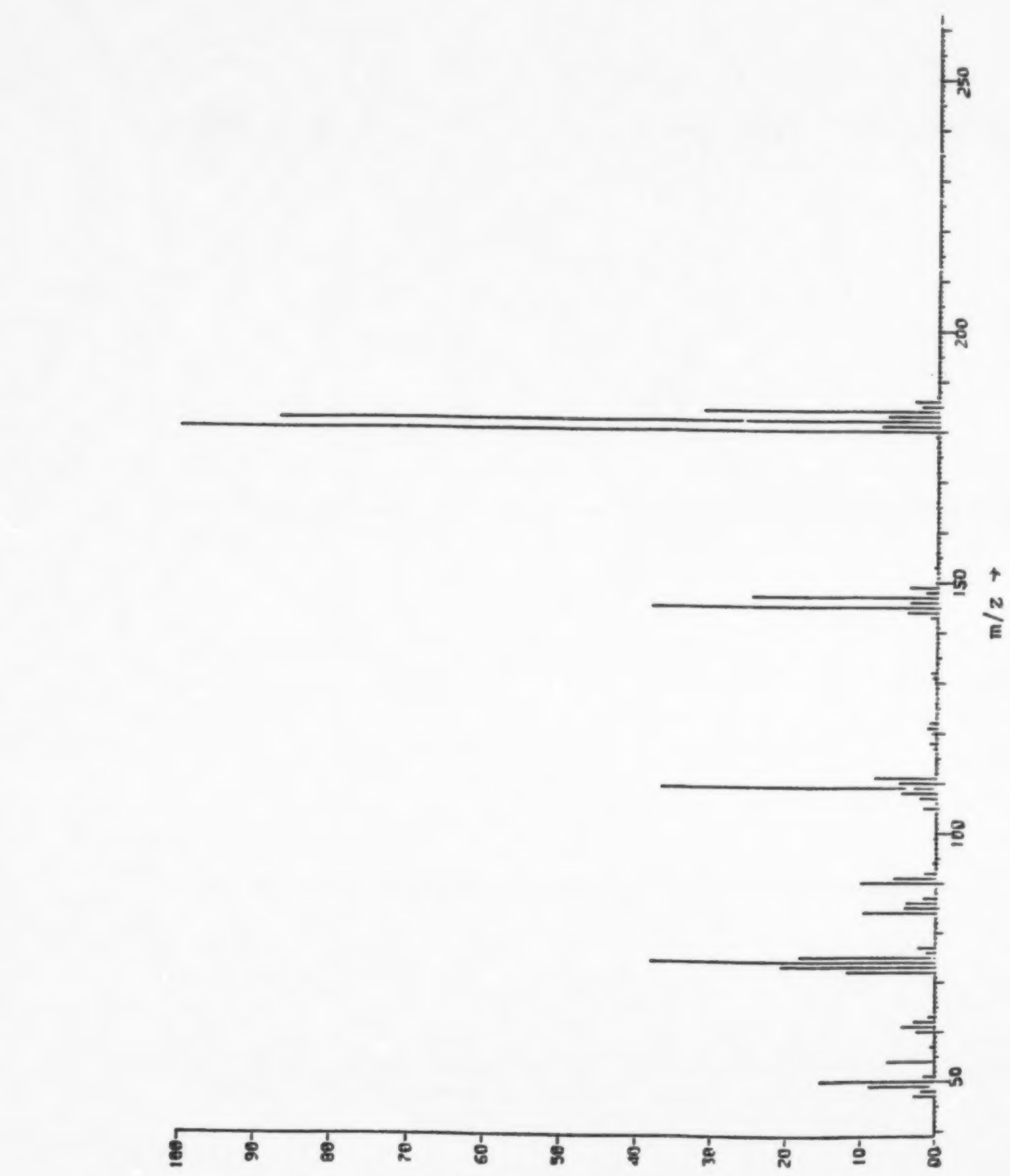


Figure C2. Mass spectrum of peak at 41.03 min.

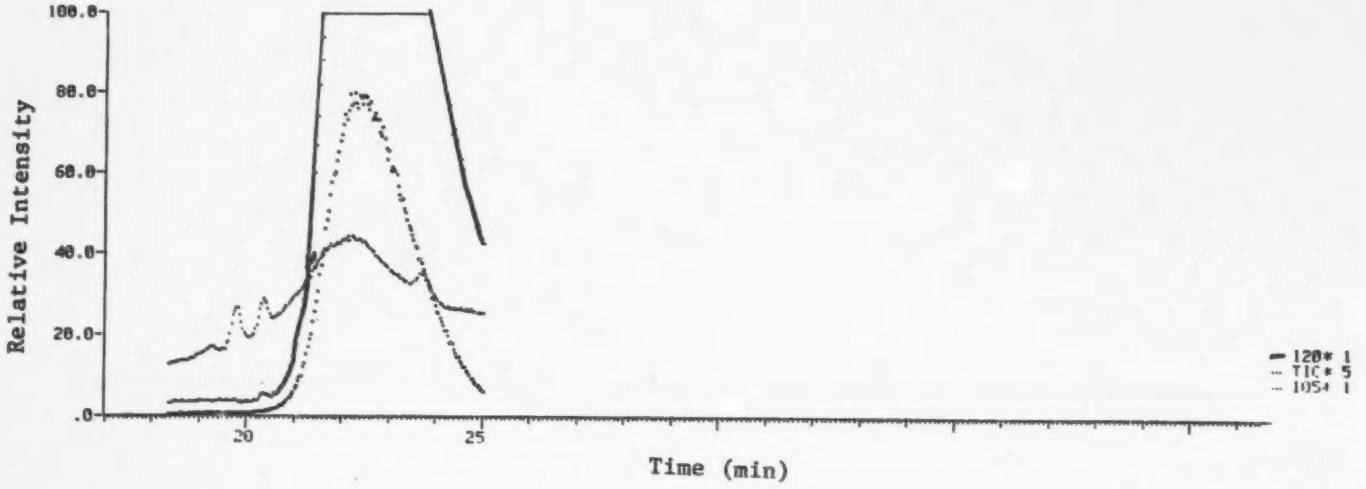


Figure C3. Mass chromatograms - m/z 120, 105.

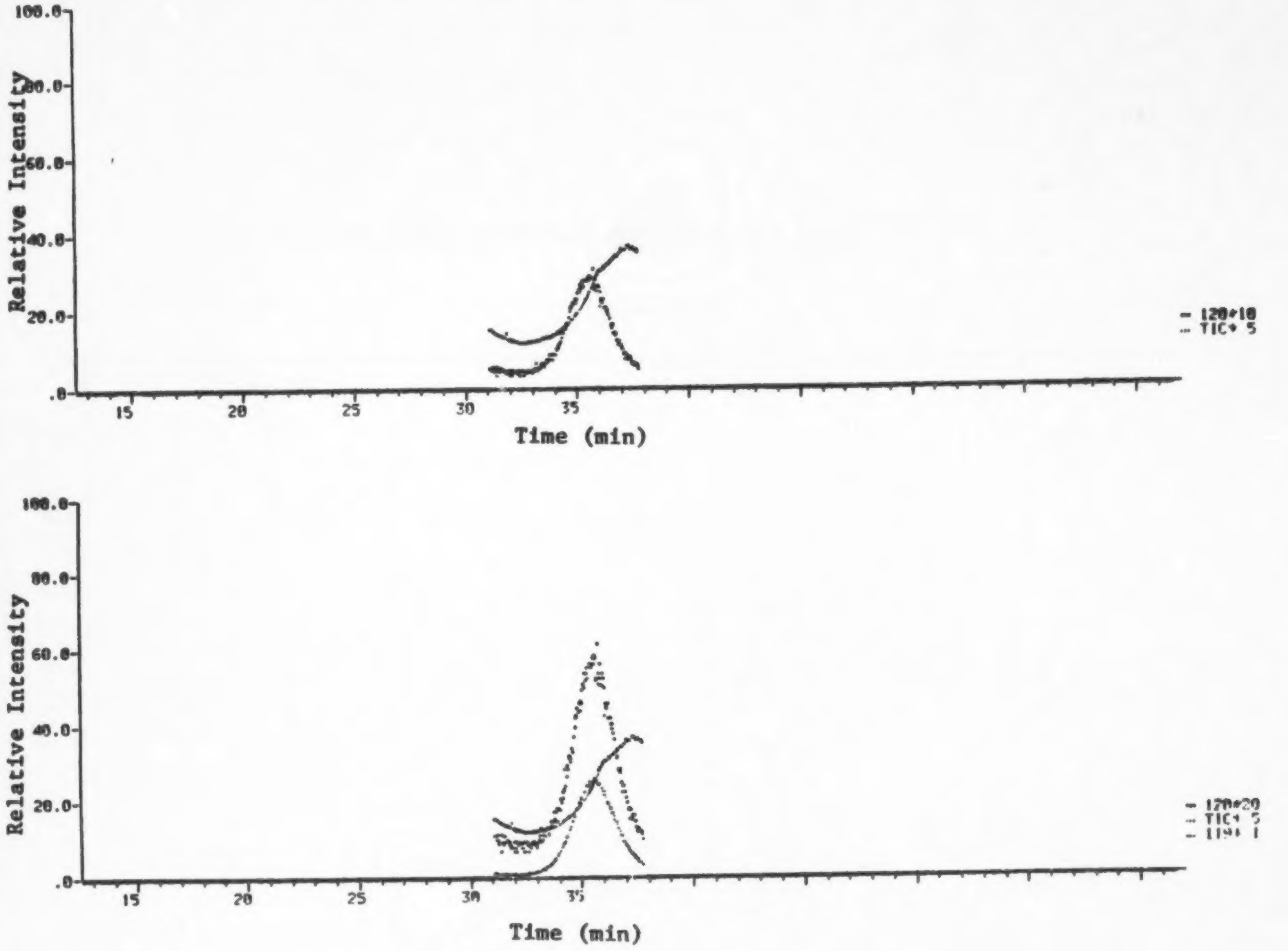


Figure C4. Mass chromatogram - m/z 120, 119.

APPENDIX D

ANALYSIS OF PRIORITY POLLUTANTS IN AIRSTREAMS FROM WASTEWATER AND ACTIVATED SLUDGE

110 SCOPE AND APPLICATION

111 This method covers the determination of volatile priority pollutants which are stripped into the air streams passing through raw wastewaters and activated sludge. The organics are adsorbed from the air onto a Tenax GC sampling cartridge (1). Recovery of the volatile priority pollutants is accomplished by thermal desorption, purging with helium into a liquid nitrogen cooled nickel capillary trap (2-6), and introducing the vapors into a gas chromatographic column where they are separated from each other (1). The characterization and quantification of the priority pollutants are accomplished by a mass spectrometry (1).

112 This method is applicable for the estimation of levels of "volatile" priority pollutants purged from raw and municipal wastewaters by process aeration. It can be used to monitor these compounds with anticipated limits of detection between 1 ng/ℓ (e.g., chlorobenzene) and 90 ng/ℓ (e.g., 1,2-dichloropropane) in air for screening survey's of municipal wastewater treatment plants.

120 SUMMARY

121 This method offers considerable analytical versitility since a gas chromatograph/mass spectrometer/computer system is used for the analysis. Interfaced with a glass jet separator, the GC/MS/COMP system is extremely sensitive and specific for the analysis of "volatile" priority pollutants in the air stream from wastewaters at municipal sewage treatment plants. The combined use of a gas chromatographic column and specific or unique ions (m/z) representing the various compounds of interest provides a relatively specific assay method for these priority pollutants (1). The procedure describes a sampling system for air streams passed through raw wastewaters and activated sludge (open and closed basins), a thermal desorption unit, GC/MS/COMP operating parameters and methods for quantification.

122 Collected samples can be stored up to approximately 3 weeks with recoveries of priority pollutants typical of those shown in Table D1. Because some of the compounds of interest may be

TABLE D1. RECOVERY OF PRIORITY POLLUTANTS FROM STORED TENAX CARTRIDGES

Priority pollutant	Percent recovery 14 da	 21 da
1,1-dichloroethylene	48 ± 12	35 ± 8
1,2-*trans*-dichloroethylene	73 ± 9	99 ± 12
1,1,1-trichloroethane	92 ± 2	ND[a]
1,2-dichloroethane	100 ± 7	122 ± 9
trichloroethylene	99 ± 9	87 ± 13
1,2-dichloropropane	86 ± 4	ND
tetrachloroethylene	97 ± 3	68 ± 3
chlorobenzene	80 ± 7	87 ± 3
bis-(2-chloroethyl)ether	86 ± 6	93
bis-(chloromethyl)ether	41 ± 4	ND
acrolein	45 ± 15	49 ± 6
acrylonitrile	ND	81 ± 6
benzene	104 ± 8	104
toluene	103 ± 3	103 ± 7
ethylbenzene	61 ± 9	65 ± 11
chlorobenzene	80 ± 7	80 ± 4
1,1-dichloroethane	102	90
bromodichloromethane	106	77
bromoform	79	ND

[a] ND = not determined.

hazardous to man, it is extremely important to exercise safety precautions in the preparation and disposal of liquid and gas standards, cleaning of used glassware, etc.

123 This method is recommended for use only by experienced sampling personnel and GC/MS/COMP analysts or under the close supervision of such qualified persons.

130 APPARATUS AND REAGENTS

131 For sampling protocol

131.1 Pyrex glass tubes - 1.5 cm i.d. x 10 cm in length

131.2 Tenax GC (35/60 mesh)

131.3 Silanized glass wool

131.4 Calcium sulfate (anhydrous)

131.5 Kimax® (2.5 cm x 1.57 cm) culture tubes

131.6 Aluminum foil and teflon-lined caps for 131.5

131.7 One gallon paint cans or equivalent

131.8 Tweezer

131.9 Kimwipes®, gum labels

132 For cartridge preparation

132.1 High purity helium gas

132.2 Clean-up solvents: (a) methanol; (b) n-pentane-both glass redistilled

132.3 Muffle furnance (range to 600°C)

132.4 Thermal desorption unit (Nutech Model 321 or equivalent)

132.5 Soxhlet apparatus

132.6 Vacuum oven

133.7 Stainless steel sieves (35/60)

133 For sampling

133.1 Nutech 221-1A sampler (Durham, NC: or equivalent)

133.2 Pyrex glass tube (Nutech 320-3-101 or equivalent - 1.5 cm i.d. x 10 cm in length)

133.3 TFE coupling (Nutech 320-3-102)

133.4 Aerosol prefilter (Nutech 320-3-104)

133.5 Quick connect (Nutech 320-3-103)

133.6 Teflon filters - 0.2 μ porosity, Gelman (2.5 cm diameter)

133.7 Aeration tank sampler - parts listed in Table D2, see Figures D1-D4 (Nutech Model 851 or equivalent)

134 For quantitation

134.1 Gas chromatograph/mass spectrometer/computer system (capable of performing functions under 170)

134.2 Gas chromatographic column materials: (a) 8 ft stainless steel x 0.1 in i.d. tube packed with Carbopak C (60/80 mesh) coated with 0.2% Carbowax 1500; (b) 1 ft stainless x 0.1 in i.d. column packed with Chromosorb W coated with 3% Carbowax 1500

134.3 Permeation tubes (see Table D3)

134.4 Permeation apparatus (see Figure D5)

134.5 Syringes - 10 μℓ volume, additional sizes may also be required

140 PREPARATION OF SAMPLING CARTRIDGES

141 Calcium sulfate is cleaned and dehydrated in a muffle furnace at 500°C for 4 hrs, cooled and kept under an argon atmosphere. Approximately 1 g $CaSO_4$ is placed at the bottom of the Kimax® sample transport tube and covered with about 2 cm of pyrex wool. Anhydrous $CaSO_4$ is used to dry the sampling cartridges after sampling "humid" air streams and the $CaSO_4$ is retained in the sample transport tubes throughout the entire storage period.

142 Virgin Tenax GC (Applied Science, State College, PA, or material to be recycled) is extracted in a Soxhlet apparatus for a minimum of 18 hrs each time with methanol and n-pentane prior to preparation of cartridge sampling tubes (Nutech Corp., Durham, NC). After purification of the Tenax GC sorbent and drying in a vacuum (∿28 in H_2O) oven at 100°C for 3-5 hrs, the sorbent is meshed to provide a 35/60 particle size range. This operation should be carried out in an atmosphere which is free of organic vapor background.

TABLE D2. PARTS LIST FOR AERATION TANK SAMPLER

Nutech part #[a]	Description	Quantity
851-001	cabinet enclosure #201-002	1
851-002	sample chamber #320-001	1
851-003	stainless sample hood	1
851-004	polyethylene foam pad	4
851-005	heated TFE sample line	1
851-006	quick connect, 1/2" female	1
851-007	quick connect, 1/2" male	1
851-008	thermocouple, type K	1
851-009	dry gas meter w/thermometer installed #221-028	1
851-010	mass flow meter	1
851-011	24 VDC power supply	1
851-012	diaphragm pump	1
851-013	temperature control board	1
851-014	relay w/socket, 110 VAC, DP	1
851-015	4 terminal barrier strip	2
851-016	switch SPST	2
851-017	fuse holder	2
851-018	LCD display	1
851-019	power cord	1
851-020	male AC connector	1
851-021	female AC connector	1
851-022	switch DPDT	1
851-023	valve, flow control	3
851-024	valve, solenoid, 110 VAC	3
851-025	stainless manifold, 4 port	1
851-026	stainless manifold, 5 port	1
851-027	check valve	1
851-028	cartridge assembly w/TFE union	3
851-029	sample manifold, 3 port TFE	1
851-030	1/4 NPT nipple, TFE	3

(continued)

TABLE D2 (cont'd.)

Nutech part #[a]	Description	Quantity
851-031	bulkhead union, 1/4"	3
851-032	stainless L	3
851-033	TFE reducer 1/2" to 7/16"	1
851-034	hose clamp, 7/16"	1
851-035	switch SPST	3
851-036	indicator lamp	1
851-037	1" foam insulation	2 ft^2
851-038	piano hinge, 8"	1
851-039	deleted	
851-040	screws, misc.	
851-041	house coupling, 1/2 NPT	17
851-042	pot, 1K, 20T	1
851-043	resistor 1%, 8.2K	1
851-044	thermocouple connector, male, type K	1
851-045	thermocouple connector, female, type K	1
851-046	thermocouple connector, mounting bracket	1
851-047	fuse, 2A	1
851-048	fuse, 3A	1
851-049	crimp terminal	30
851-050	vinyl tubing 3/16 x 5/16"	15 ft
851-051	vinyl tubing 7/16 x 5/8"	3 ft
851-052	cabinet base #201-001	1
851-053	control panel #201-004	1
851-054	cabinet handles #201-008	3
851-055	knockout jar	1

[a] or its equivalent.

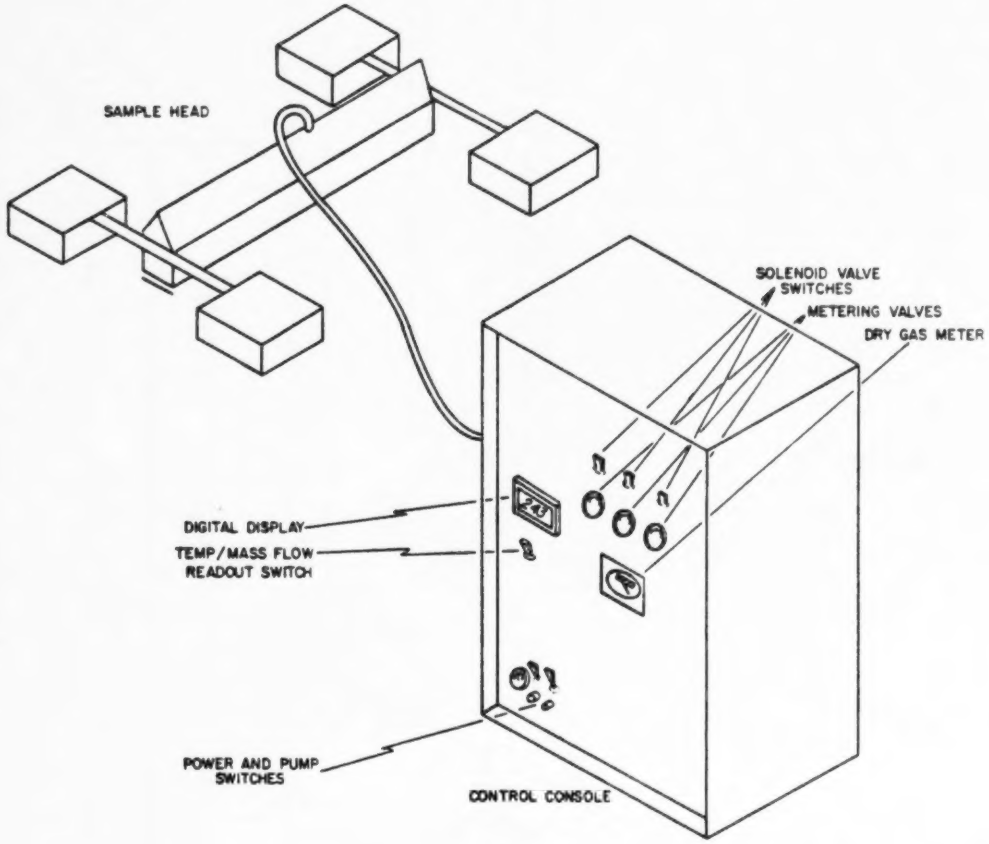

SAMPLE HEAD
SOLENOID VALVE SWITCHES
METERING VALVES
DRY GAS METER
DIGITAL DISPLAY
TEMP/MASS FLOW READOUT SWITCH
POWER AND PUMP SWITCHES
CONTROL CONSOLE

Figure D1. Schematic of sampler system for grit chambers and aeration tanks.

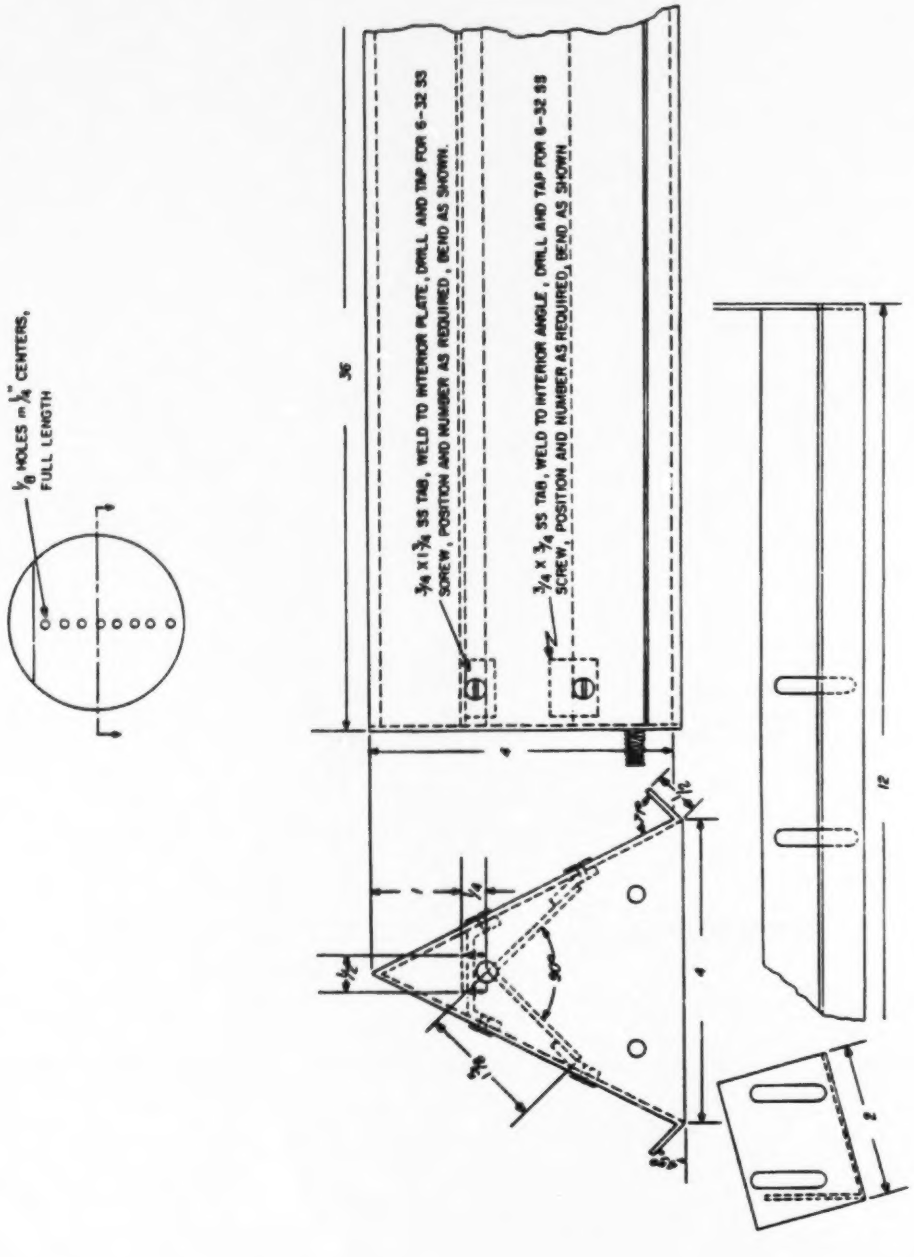

1/8 HOLES @ 1/4" CENTERS, FULL LENGTH
36
3/4 X 1 3/4 SS TAB, WELD TO INTERIOR PLATE, DRILL AND TAP FOR 6-32 SS SCREW, POSITION AND NUMBER AS REQUIRED, BEND AS SHOWN.
3/4 X 3/4 SS TAB, WELD TO INTERIOR ANGLE, DRILL AND TAP FOR 6-32 SS SCREW, POSITION AND NUMBER AS REQUIRED, BEND AS SHOWN
4
4
12
2
90°
1/2
1/4
1

Figure D2. Schematic of sampling shroud.

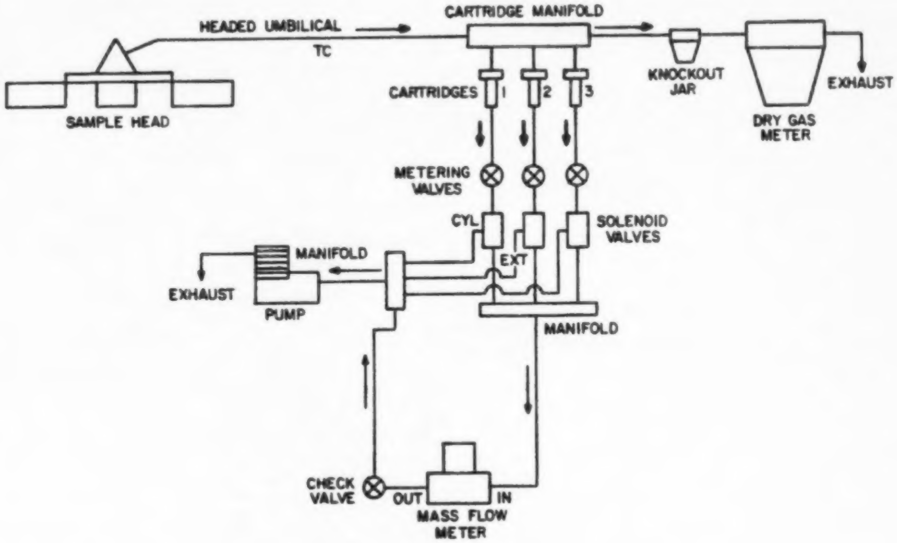

HEADED UMBILICAL
TC
CARTRIDGE MANIFOLD
SAMPLE HEAD
CARTRIDGES
1
2
3
KNOCKOUT JAR
DRY GAS METER
EXHAUST
METERING VALVES
CYL
SOLENOID VALVES
EXT
MANIFOLD
EXHAUST
PUMP
MANIFOLD
CHECK VALVE
OUT
IN
MASS FLOW METER

Figure D3. Diagram of pneumatics in sampler system.

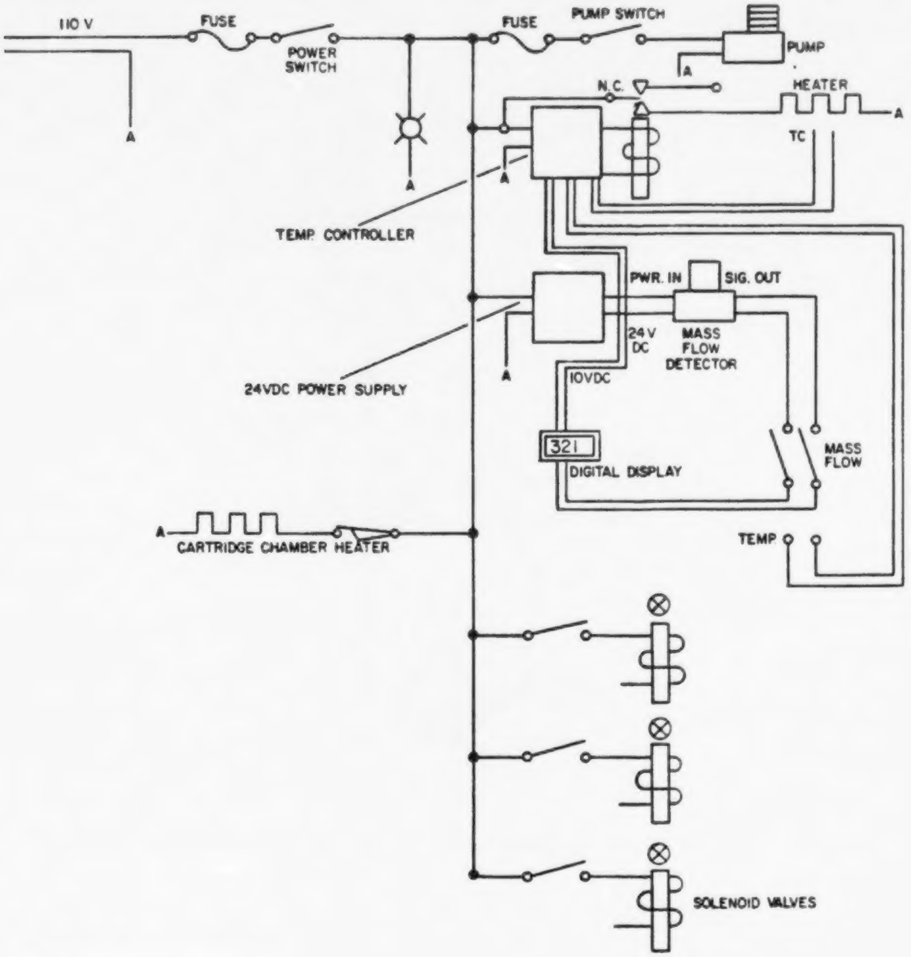

110 V
FUSE
POWER SWITCH
FUSE
PUMP SWITCH
PUMP
A
N.C.
HEATER
TC
TEMP. CONTROLLER
PWR. IN
SIG. OUT
24 V DC
MASS FLOW DETECTOR
24VDC POWER SUPPLY
10VDC
321
DIGITAL DISPLAY
MASS FLOW
TEMP
CARTRIDGE CHAMBER HEATER
SOLENOID VALVES

Figure D4. Schematic of electronics in sampler system.

TABLE D3. PERMEATION TUBES FOR SEVERAL VOLATILE PRIORITY POLLUTANTS (1)

Priority pollutant	Permeation tube		Approximate rate g/min
	Dimensions (O.D. x I.D. x length, cm)	Material	
methyl choride	0.64 x 0.48 x 6.5	FEP	1.8×10^{-6}
dichlorodifluoromethane	Unknown		
methylbromide	0.64 x 0.48 x 6.0	FEP	1.2×10^{-6}
vinyl chloride	0.64 x 0.48 x 10.0	FEP	2.0×10^{-6}
chloroethane	Unknown		
dichloromethane	0.64 x 0.48 x 11.0	FEP	7.0×10^{-7}
trichlorofluoromethane	Unknown		
1,1-dichloroethylene	0.64 x 0.48 x 10.1	TFE	1.0×10^{-6}
1,1-dichloroethane	0.64 x 0.48 x 9.9	TFE	4.2×10^{-7}
1,2-trans-dichloroethylene	0.64 x 0.48 x 10.0	TFE	1.1×10^{-5}
chloroform	0.64 x 0.48 x 11.0	FEP	6.4×10^{-8}
1,2-dichloroethane	0.64 x 0.48 x 8.0	TFE	4.0×10^{-7}
1,1,1-trichloroethane	0.64 x 0.48 x 8.0	TFE	9.1×10^{-8}
carbon tetrachloride	0.64 x 0.48 x 9.9	TFE	3.0×10^{-8}
bromodichloromethane	0.64 x 0.48 x 5.2	TFE	1.1×10^{-7}
bis-(chloromethyl) ether	Unknown		
1,2-dichloropropane	0.64 x 0.48 x 7.7	TFE	9.8×10^{-8}
1,3-trans-dichloropropane	Unknown		
trichloroethylene	0.64 x 0.48 x 10.0	TFE	2.2×10^{-6}
dibromochloromethane	Unknown		
1,3-cis-dichloropropene	Unknown		
1,1,2-trichloroethane	0.64 x 0.48 x 10.3	TFE	6.2×10^{-8}
benzene	0.64 x 0.32 x 0.6	PE	7.1×10^{-6}
2-chloroethylvinyl ether	Unknown		
bromoform	0.64 x 0.48 x 5.1	PE	2.5×10^{-5}
1,1,2,2-tetrachloroethene	0.64 x 0.48 x 5.2	TFE	3.6×10^{-7}
1,1,2,2-tetrachloroethane	0.64 x 0.32 x 7.0	PE	9.7×10^{-6}
toluene	0.64 x 0.48 x 7.0	TFE	1.9×10^{-7}
chlorobenzene	0.64 x 0.48 x 5.5	TFE	2.0×10^{-7}
ethyl benzene	0.64 x 0.48 x 12.7	TFE	6.8×10^{-8}
acrolein	0.64 x 0.48 x 10.0	TFE	1.3×10^{-6}
acrylonitrile	0.64 x 0.48 x 10.4	TFE	1.0×10^{-6}
bis-(2-chloroethyl)ether	0.64 x 0.48 x 8.3	TFE	1.0×10^{-10}
perfluorotoluene	0.64 x 0.48 x 7.2	FEP	8.94×10^{-6}
1,3-dichlorobenzene	0.64 x 0.32 x 9.0	PE	1.1×10^{-7}
perfluorobenzene	0.64 x 0.48 x 5.5	FEP	8.5×10^{-6}

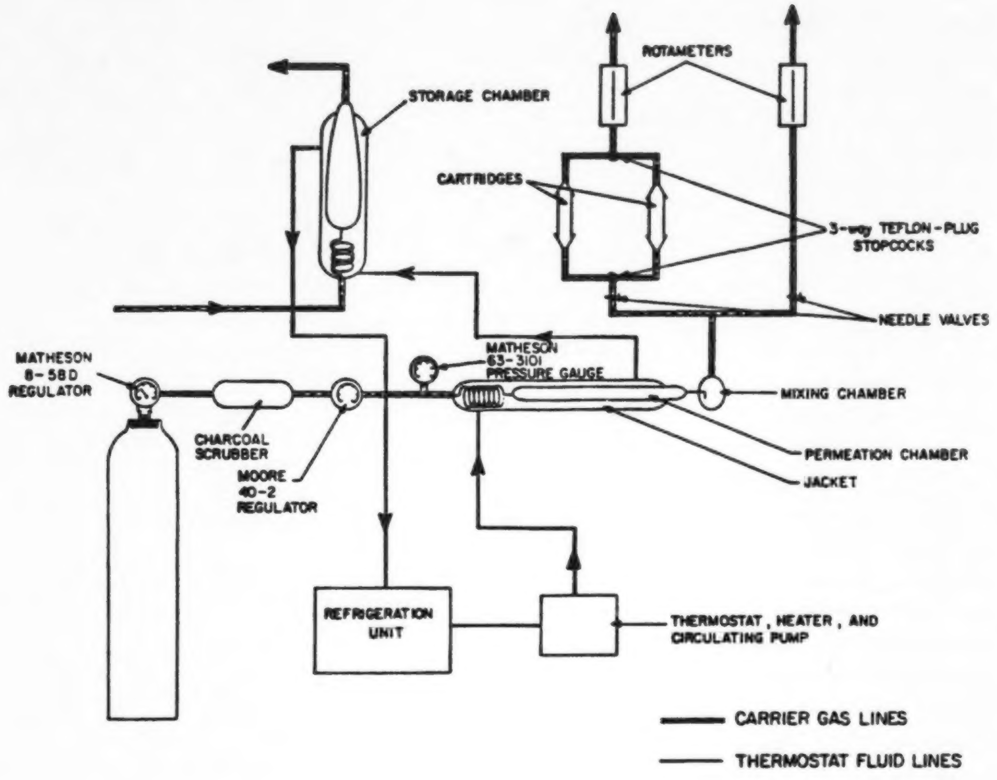

ROTAMETERS
STORAGE CHAMBER
CARTRIDGES
3-way TEFLON-PLUG STOPCOCKS
NEEDLE VALVES
MATHESON 8-58D REGULATOR
MATHESON 63-3101 PRESSURE GAUGE
MIXING CHAMBER
CHARCOAL SCRUBBER
MOORE 40-2 REGULATOR
PERMEATION CHAMBER
JACKET
REFRIGERATION UNIT
THERMOSTAT, HEATER, AND CIRCULATING PUMP
CARRIER GAS LINES
THERMOSTAT FLUID LINES

Figure D5. Permeation system for generating air/vapor mixtures (1).

143 Sampling tubes are prepared by packing in a 10 cm long x 1.5 cm i.d. glass tube 6 cm of 35/60 mesh Tenax GC with glass wool in the ends to provide support (1). Cartridge samplers are then conditioned at 270°C with helium flow at 30 ml/min for 1 hr. The conditioned cartridges are transferred to Kimax® (2.5 cm x 150 cm) culture tubes (or Nutech sample cartridge transport tubes, Fig. D6), packed with glass wool to prevent breakage, immediately sealed using Teflon-lined caps (with no adhesive binders) and cooled. Culture tubes containing the cartridges are immediately placed in a metal container (equivalent to a paint can) which has a pressure sealable cap. This procedure is performed in order to avoid recontamination of the sorbent bed (1,6,7). The sampling cartridges can be stored under these conditions for a period of about 3 wks prior to sampling.

150 SAMPLING AND PRESERVATION

151 Integrated sampling of the air stream passing through wastewaters at municipal treatment plants is accomplished using a prototype Nutech Model 851 or equivalent sampler (Nutech Corp., Durham, NC). Flow rate regulation between 5-300 ml/min is necessary. Flow rates are maintained at prescribed rates using variable critical orifices for the three sampling cartridges. The individual or total flow through the cartridges is monitored with a calibrated mass flow meter. The total flow from the aeration basin (minus the sampling volume) is registered by a dry gas meter; only a fraction (up to 30%) of the air stream passing through the sampling unit is sampled by the Tenax GC cartridges.

151.1 Figure D1 depicts the sampling unit. The sampling unit consists of a gas sampling head, a sample transfer line and a gas sampling manifold. A Teflon® manifold is used to distribute the air stream to three replicate Tenax GC cartridges; the remaining gas flow is measured with a dry gas meter (Fig. D1). The sampling cartridges are housed in a constant temperature bath (70°F) in order to ensure uniform and constant breakthrough volumes for the priority pollutants throughout the entire sampling period.

151.2 The sampling head (Fig. D2) is constructed of 316 stainless steel for corrosion resistance. The sampling area is approximately 1 ft^2 (4 in x 36 in). Internal baffles inhibit entry of fluid into the transfer line (Fig. D2). During operation, bubbles rising from aeration pipes are trapped in a closely defined shroud designed to maintain an accurate sample area. The shroud is 16 gauge stainless steel so that only those bubbles rising within the defined area are collected. Once trapped in the shroud, the bubbles create a positive gas pressure forcing the gases through the heated transfer line (40°C) to the sampler.

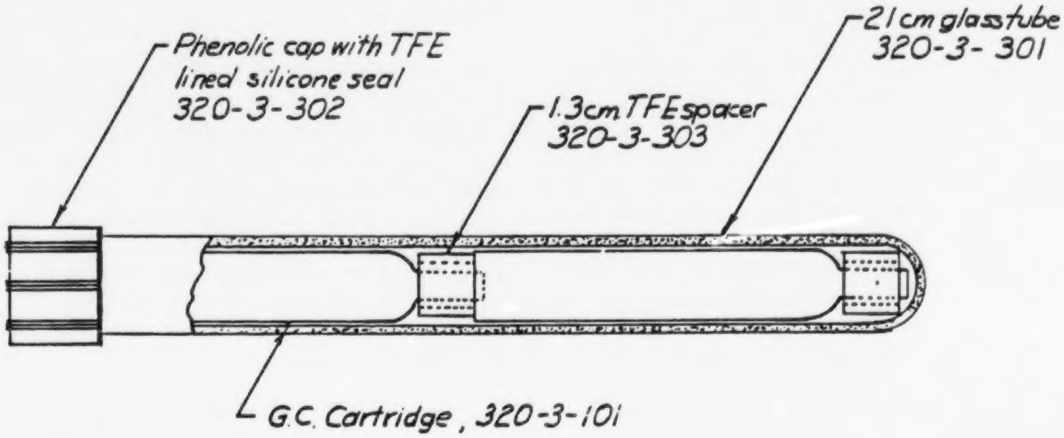

Phenolic cap with TFE
lined silicone seal
320-3-302
1.3cm TFE spacer
320-3-303
21 cm glass tube
320-3-301
G.C. Cartridge, 320-3-101

Figure D6. Sampler cartridge transport tube (Nutech Corp., Durham, NC).

151.3 For typical operating conditions in open grit chambers and activated sludge ponds, the gas sampling head is placed on the wastewater which is supported by a flotation collar and held in a fixed position by the support arms fastened to guardrails. For some aeration rates through the activated sludge, the gas flow is approximately 2.5 ℓ/min/ft^2 surface area. This rate can be highly variable; however, it can be easily determined prior to sampling by simply passing the total flow through the dry gas meter for a short period of time (∿10 min).

151.4 In general, a sampling volume of 1 ℓ/cartridge is sufficient for achieving 1 ppb sensitivity. Thus, the sampling rate is adjusted to accommodate the desired sampling period. Triplicate cartridges are deployed on each sampling unit.

151.5 Larger volumes may be taken; however, the quantity of pollutants accumulated on the sampling cartridges may ultimately saturate the GC/MS/COMP system. For larger sample volumes, it is important to realize that the total volume of air sampled may cause the elution of a few of the priority pollutants possessing low breakthrough volumes (Table D4). These breakthrough volumes have been determined by a previously described technique (8). The breakthrough volume has been defined as that volume which causes 50% of a discrete sample introduced into the cartridge to pass through the cartridge and be lost.

152 Continuous sampling for priority pollutants in the vents from closed chambers is accomplished using a Nutech Model 221-1A portable sampler of equivalent (Nutech Corp., Durham, NC; Fig. D7). Flow rates between 10-300 ml/min are available with this sampling system when using critical orifices. The total flow is monitored through a calibrated flow meter to integrate the flow sampled from all cartridges. The portable sampling unit operates on a 12 v storage battery and is capable of continuous operation for a period of 24 hr. However, in most cases at the rates which are employed for sampling of the vent gas from the closed chambers, the sampling period may be adjusted between 10 min and 3 hr. Replicate cartridges may be deployed on each sampling unit utilizing a sampling head or manifold. The sampling head should be connected to a vacuum line of approximately 20 ft so that the sampler can be positioned at a distant location from the vent gas unless the sampler itself is made explosion-proof. The suggested sample volume is 1 ℓ as described under 151.3. Larger sample volumes may be taken if desired while considering breakthrough volumes given in Table D4.

153 All Tenax GC sampling cartridges once prepared for field sampling must be kept tightly closed in a double container as described earlier (143). At the point when sampling is to begin, they are

TABLE D4. BREAKTHROUGH VOLUMES FOR SEVERAL PRIORITY POLLUTANTS[a] (1)

Priority pollutants	B.P.	Breakthrough Volume										
		Temperature °F (°C)										
		50(10)	55(12.7)	60(15.5)	65(18.3)	70(21.1)	75(23.9)	80(26.7)	85(29.4)	90(32.2)	95(34.9)	100(37.8)
1,1-dichloroethylene	32	2.4	2.2	1.8	1.6	1.4	1.3	1.2	1.1	1.0	0.97	0.87
dichloromethane	40	14	12	9.7	8.3	6.9	5.9	4.9	4.1	3.5	2.9	2.4
1,2-*trans*-dichloroethylene	47.5	1.90	1.81	1.73	1.68	1.65	1.51	1.44	1.38	1.31	1.25	1.20
1,1-dichloroethane	57	8.9	7.9	7.0	6.3	5.6	5.0	4.5	3.9	3.5	3.1	2.7
chloroform	61.2	17	14	12	10	9.1	7.7	6.6	5.6	4.8	4.2	3.5
1,1,1-trichloroethane	74	23	21	18	16	15	14	12	10	9	8	7
carbon tetrachloride	76.8	41	34	29	24	20	17	14	12	10	8	7
1,2-dichloroethane	84	49	42	36	31	27	23	20	17	15	12	11
trichloroethylene	87	90	78	67	58	50	44	38	33	28	24	21
bromodichloromethane	90	83	70	61	52	45	39	34	29	25	22	19
1,2-dichloropropane	96.2	229	199	162	138	115	98	81	69	58	49	41
1,1,2-trichloroethane	113	309	245	208	177	151	128	109	93	79	67	57
tetrachloroethylene	121	361	361	267	250	196	170	144	125	106	92	78
chlorobenzene	132	899	776	653	563	473	408	344	296	249	215	181
1,1,2,2-tetrachloroethane	146	477	406	353	308	262	228	199	173	147	128	112
bromoform	149.5	511	445	388	330	287	245	213	186	158	138	117
1,3-dichlorobenzene	172	2,393	2,075	1,758	1,524	1,291	1,119	948	885	697	603	510
1,4-dichlorobenzene	174	2,390	2,071	1,752	1,520	1,289	1,113	937	812	688	592	497
bis-(2-chloroethyl)ether	178	1,692	1,440	1,226	1,043	888	768	653	560	477	406	354
1,2-dichlorobenzene	179	2,422	2,191	1,960	1,716	1,463	1,301	1,139	989	839	769	699
acrolein	52	1.9	1.8	1.7	1.5	1.4	1.3	1.2	1.1	1.0	0.91	0.83
acrylonitrile	77	8.5	7.4	6.6	5.7	5.0	4.4	3.9	3.4	3.0	2.6	2.3
benzene	80	108	92	77	65	54	46	38	32	27	23	19
toluene	110.6	494	421	348	296	245	209	173	147	122	104	86
ethylbenzene	136	1,393	1,188	984	838	693	590	487	415	344	293	243

[a] Breakthrough volume is in ℓ/cartridge (1.5 cm i.d. x 6.0 cm bed of 35/60 mesh Tenax GC).

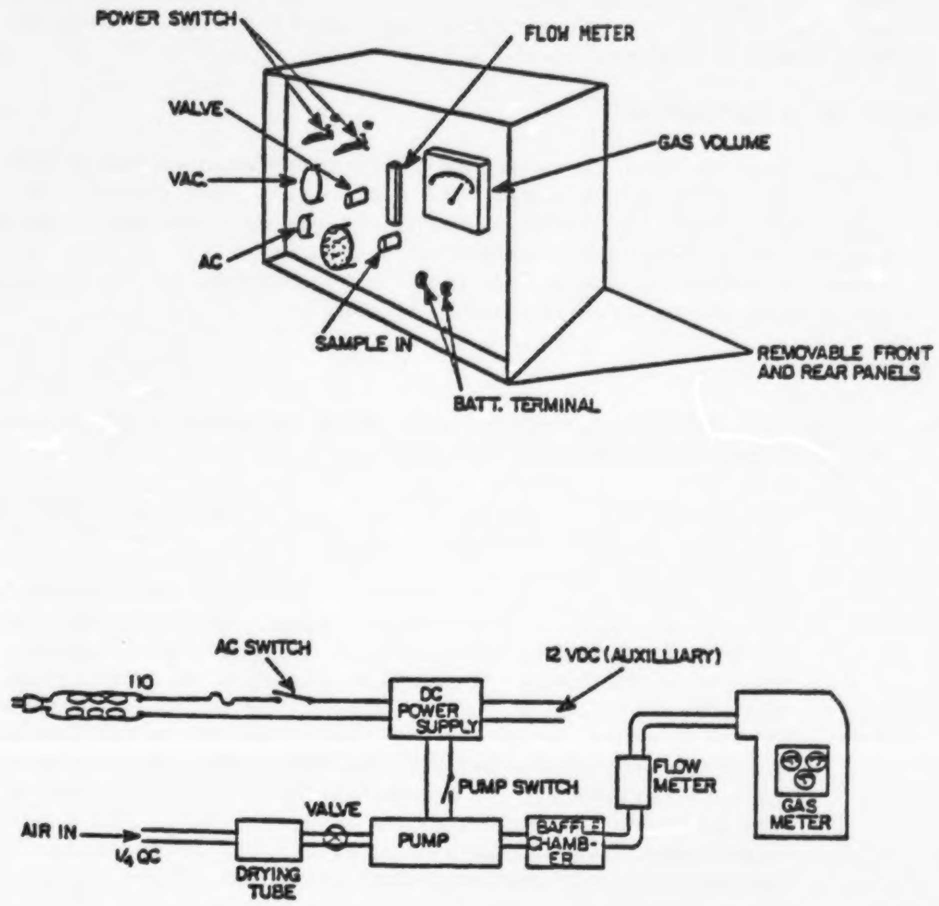

POWER SWITCH
FLOW METER
VALVE
GAS VOLUME
VAC.
AC
SAMPLE IN
REMOVABLE FRONT AND REAR PANELS
BATT. TERMINAL
AC SWITCH
110
12 VDC (AUXILLIARY)
DC POWER SUPPLY
PUMP SWITCH
FLOW METER
GAS METER
AIR IN
1/4 QC
VALVE
PUMP
BAFFLE CHAMBER
DRYING TUBE

Figure D7. Sampler schematic for closed chamber systems.

to be removed from their respective containers and handled with Kimwipes®. After sampling is completed, the cartridges are returned immediately to their containers, and coded on the label which is affixed to the container. Samples are stored at -20°C in sealed paint cans until ready for analysis. Experiments have been conducted which demonstrate that the priority pollutant vapors collected on Tenax GC sorbent are stable and can be quantitatively recovered from the cartridge samplers up to 3 weeks after sampling when they are tightly closed in sample cartridge holders and placed in a second container that can be sealed, protected from light and stored at -20°C (1).

160 REMOVAL OF INTERFERENCES

161 At the present time there are no known interferences using the described collection and analysis system (1). The use of the specified packed gas chromatographic column in combination with single ion (m/z) plots provides sufficient specificity for the direct analysis of "volatile" priority pollutants on the Tenax GC cartridges without further purification.

170 QUANTITATION

171 For quantitative measurements this method requires a gas chromatography/mass spectrometer/computer.

171.1 The operation of the GC/MS/COMP system typically requires the mass spectrometer to be first set to operate in the repetitive scanning mode. In this mode the magnetic sector or quadrupole is automatically scanned upward from a preset low mass to a high mass value. Although the scan range may be varied depending on the particular sample, typically the range is set from m/z 25 to m/z 300. The scan is completed in approximately 1.0 sec. At this time the instrument automatically resets itself to the low mass position in preparation for the next scan, and the information is accumulated by an on-line dedicated computer and written onto either a disk or magnetic tape. The scan plus reset period should be approximately 2.0 sec/scan cycle, and repetitively executed throughout the chromatographic run. The results are the accumulation of a continuous series of mass spectra throughout the chromatographic run in a sequential fashion.

171.2 Prior to running unknown samples, the system is calibrated daily by introducing a standard substance perfluorokerosene (magnetic sector) or heptacosafluorotributylamine (quadrupole) into the instrument. The calibration curve which is thus generated is stored in the computer memory. This calibration serves only to calibrate the masses over the mass scanning range.

172 The preparation of standards is required for calibrating the GC/MS/COMP system for quantitative analysis of priority pollutants. It is necessary to accurately spike Tenax GC sampling cartridges with known amounts of priority pollutants and the internal standards, perfluorobenzene and perfluorotoluene, utilizing the permeation system described earlier.

173 The permeation tubes must be gravimetrically calibrated (1,5,6,8). In general, 500-1,000 ng of each priority pollutant is spiked onto the Tenax GC cartridge along with a known quantity of internal standards perfluorobenzene and perfluorotoluene (suggested concentrations of 500 ng/cartridge).

174 The instrumental conditions for the analysis of priority pollutants collected on a sorbent Tenax GC sampling cartridge are given in Table D5. The inlet manifold (Nutech Model 321) consisting of a thermal desorption chamber and a six-port Valco valve (Valco Inst. Corp., Houston, TX) is maintained at 270°C. The glass jet separator (or equivalent) is maintained at 250°C. The mass spectrometer is set to scan the mass range from 25-300 daltons. The helium purge gas through the desorption chamber is adjusted to 15 ml/min. The nickel capillary trap on the inlet manifold is cooled with liquid nitrogen. In a typical thermal desorption cycle, a sampling cartridge (which has come to room temperature) is placed in the preheated desorption chamber and the helium gas is passed through the cartridge to pu[illegible] the priority pollutant vapors into the liquid nitrogen capillary trap [the inert activity of the trap has been shown in previous studies (2-8)]. While the magnetic or quadrupole instrument is continuously scanning, and after desorption has been completed, the six-port valve is rotated, the temperature on the capillary loop is rapidly raised (>150°/min), and automatic data acquisition is initiated. The carrier gas then introduces the vapors onto the gas chromatographic column. The chromatographic column is held for 3 min at 60°C, programmed 8°C/min to 160°C, and held until all compounds have eluted. After all the components have been eluted from the gas chromatographic column, the analytical column is then cooled to 60°C, and the next sample is processed.

175 Upon completion of the chromatographic run, there are from 800-1,400 spectra accummulated on the disk or magnetic tape which are then subsequently processed. Depending on the information required that day, data may then either be processed immediately, or additional samples may be run, stored on magnetic tape, and the results examined at a later time.

175.1 The mass spectra are processed in the following manner: first, the original spectra are scanned, and the integrated ion current information is extracted, then reconstructed chromatograms are plotted (total ion intensity against the spectrum number or elapsed time) on an electrostatic recorder. The information will generally indicate whether the

TABLE D5. OPERATING PARAMETERS FOR GC-MS-COMP SYSTEM (1)

Parameter	Setting
Inlet-manifold[a]	
desorption chamber and valve	270°C
capillary trap - trap cycle	-195°C
inject cycle	+250°C
thermal desorption time	8 min
He purge rate	15 ml/min
GC	
column	60-160°C, 8°/min
He carrier flow	40 ml/min
GC/MS interface (glass jet separator, transfer line)	250°C
MS[b]	
scan range	*m*/*z* 25→300
scan cycle rate, automatic cyclic	∿2 sec
emission current	500 μA
electron energy	70 eV
ion energy	6 v
lens voltage	-100 v
extractor voltage	8 v
samples/dalton	1

[a] Available from Nutech Corp., Durham, NC.

[b] Conditions for quadrupole instrument.

run is suitable for further processing since it provides some idea of the number of unknowns in the sample and the resolution obtained using the particular GC column conditions.

175.2 For the magnetic sector instruments, the next stage of processing generally involves the mass conversion of the spectral peak times to peak masses which is done directly via the dual disk system. A mass conversion is accomplished by use of the calibration table obtained previously using perfluorokerosene. Normally, one set of the calibration data is sufficient for an entire day's data processing since the characteristics of the Hall probe used are such that a variation in calibration is <0.2 daltons/day. For quadrupole instruments, it may be necessary to check the calibration more frequently throughout the analysis period.

175.3 In many cases an estimation of the level of priority pollutants by gas chromatography in combination with mass spectrometry is not feasible utilizing only the total ion current. Since baseline resolution between peaks is not always achieved, the techniques suggested are those whereby full spectra are obtained during the chromatographic separation step, and the selected ions are presented as single ion plots using computer software programs. This allows the possibility of deconvoluting constituents which are not resolved in the total ion current chromatogram (1). Single ion plots may be used for any combination of $\underline{m}/\underline{z}$ ions given in Table D6 when full spectra are obtained during chromatography. Thus, selectivity is increased by using a unique ion for that particular priority pollutant, and its intensity (peak height or area) is used for quantification. Quantification is achieved using standards which are loaded onto the sampling cartridges prior to instrumental analysis, and ratioing the intensity of the priority pollutants ($\underline{m}/\underline{z}$) to that of the perfluorobenzene and perfluorotoluene ($\underline{m}/\underline{z}$).

176 An example of the analysis of priority pollutants from an aeration system is shown in Figures D8 and D9, and the background from a blank Tenax GC cartridge is shown in Figure D10. The tandem chromatographic columns coated with Carbowax 1500 on Carbopak C and Chromosorb W are capable of partially resolving the priority pollutants. The final requisite resolution is achieved through single ion profiles.

180 QUALITY ASSURANCE

181 Standard quality assurance practices should be used with this method. Blank Tenax GC cartridges must be provided with each set of sampling cartridges that are transported to and from the sampling site. Approximately 10% of the total Tenax GC cartridges taken to the field should be set aside as blanks. During

TABLE D6. CHARACTERISTIC M/Z IONS SELECTED FOR QUANTIFICATION OF PRIORITY POLLUTANTS (1)

Priority pollutant	M.W.	1st Ion	2nd Ion	3rd Ion
		m/*z* (I)	*m*/*z* (I)	*m*/*z* (I)
chloromethane	50.5	50(100)	52(33)	-
dichlorodifluoromethane	120.9	101(13)	103(9)	87(33)
bromomethane	95.0	94(100)	86(94)	-
vinyl chloride	62.5	62(100)	64(33)	-
chloroethane	64.5	64(100)	66(33)	-
dichloromethane	84.9	84(86)	86(55)	49(100)
trichlorofluoromethane	137.4	101(100)	103(66)	-
1,1-dichloroethylene	97	86(80)	93(53)	61(100)
1,1-dichloroethane	99	63(100)	65(33)	83(13)
1,2-*trans*-dichloroethylene	97	96(90)	61(100)	98(57)
chloroform	119.4	83(100)	85(66)	-
1,2-dichloroethane	99	98(23)	100(15)	62(100)
1,1,1-trichloroethane	133.4	97(100)	99(66)	-
carbon tetrachloride	153.8	117(100)	119(96)	121(30)
bromodichloromethane	163.9	127(13)	129(17)	85(66)
bis-(chloromethyl)ether	115.0	79(100)	81(33)	-
1,2-dichloropropane	113	112(4)	114(3)	65(33)
trans-1,3-dichloropropene	113	75(100)	77(33)	-
trichloroethylene	113.4	130(90)	132(85)	97(66)
dibromochloromethane	208.3	127(78)	208(13)	206(10)
cis-1,3-dichloropropene		75(100)	77(33)	-
1,1,2-trichloroethane	113.4	97(100)	99(63)	132(9)
benzene	78.1	78(100)	79(6)	-
2-chloroethylvinyl ether	106.6	106(18)	63(95)	-
bromoform	252.8	173(100)	175(50)	252(11)
1,1,2,2-tetrachloroethylene	165.8	165(78)	166(100)	129(64)
1,1,2,2-tetrachloroethane	167.9	168(6)	137(7)	133(7)
toluene	92.1	91(100)	92(78)	-
chlorobenzene	112.6	112(100)	114(33)	-

(continued)

TABLE D6 (cont'd.)

Priority pollutant	M.W.	1st Ion m/z (I)	2nd Ion m/z (I)	3rd Ion m/z (I)
ethylbenzene	106.2	106(33)	91(100)	-
acrolein	56.1	56(83)	55(65)	-
acrylonitrile	53	53(99)	52(75)	51(32)
perfluorobenzene	186	186(100)	-	-
perfluorotoluene	235	186(100)	263(100)	117(13)
1,2-dichlorobenzene		146(100)	150(10)	-
1,3-dichlorobenzene		146(100)	150(11)	-

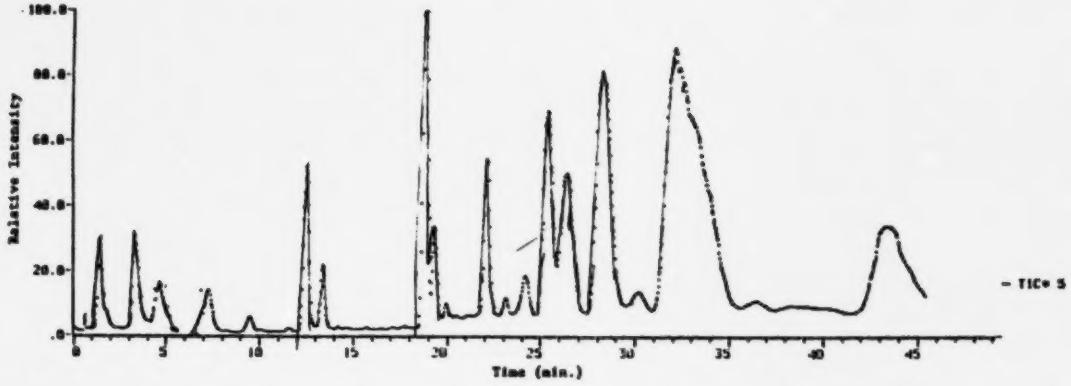


Figure D8. Total ion current profile for volatile priority pollutants collected from air stream through raw wastewater at South Burlington, NC waste treatment plant.

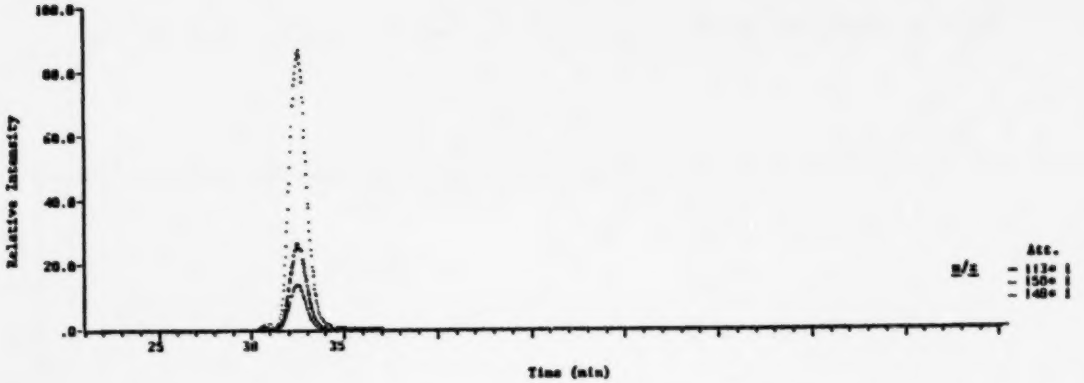


Figure D9. Ion chromatograms for 1,2-dichlorobenzene in sample taken from air stream through raw wastewater at South Burlington, NC waste treatment plant (see Figure D8).

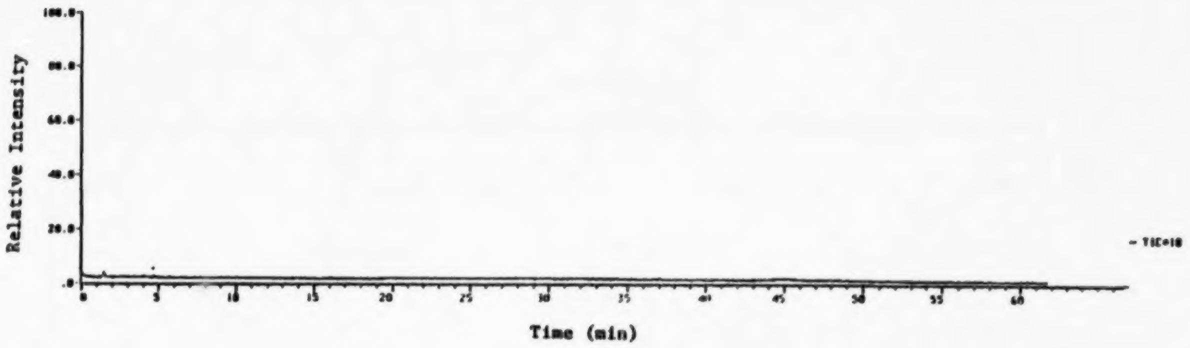


Figure D10. Total ion current profile of Tenax cartridge blank.

instrumental analysis a blank is analyzed first and then one is analyzed after every tenth sample. Likewise a control cartridge which contains known quantities of priority pollutants and has been transported to and from the sampling site as well as stored under the same conditions as the samples is to be analyzed after each blank. In this manner, RMR factors are generated from 10% of all the samples which are analyzed and provide the ability to calculate an average RMR value for each priority pollutant throughout the sample analysis period.

182 Field replicates (three) should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis and for determining the relative molar response factors (RMR). Where doubt exists over the identification of a peak from single ion plots, confirmation should be accomplished by comparing the observed ion intensity ratios of the priority pollutants in the collected sample with those observed for the authentic compound and/or the comparison of both mass spectra.

183 A sampling protocol such as that shown in Figure D11 should be used to document the history and provide the necessary information concerning each Tenax GC cartridge used. Sampling protocols are to be filled out in duplicate so that a backup record is available in the event of the loss of the original protocol. A sample code is generated as shown on the sampling protocol (Fig. D11) which is placed on the sample container of the Tenax GC cartridge and it and the chain of custody form (Table D7) are concurrently transferred with the sample from one analyst to the next throughout the collection and analysis procedure.

190 CALCULATIONS AND REPORTING

191 In order to eliminate the need to obtain complete calibration curves for each priority pollutant for which quantitative information is desired, the method of relative molar response (RMR) factors is used (7,8). Successful use of this method requires information on the exact amount of standard added and the relationship of RMR (unknown) to the RMR (standards). The method of calculation is as follows:

$$(1)\quad RMR_{\text{unknown/standard}} = \frac{A_{\text{unk}}/\text{Moles}_{\text{unk}}}{A_{\text{std}}/\text{Moles}_{\text{std}}}$$

A = peak area, determined by integration or triangulation.

The value of RMR is determined from at least three independent analyses.

Date: 8/18/79

Project No. (1 6 3 7)
Operator (E P)
Trip No. 1
Sampler (N U)
Area North Carolina (N C)
Address Highway 55 (H 5)
Period (1)
Site Parkwood (P A K)
Location (1)
Sample Code 1637-EP-1-NUNCH51PAK1

Nutech 221 (NU)
DC amps 2.5
Sampling rate 0.05 (ℓpm)
Vacuum 3 (^{11}Hg)
End: Time 0921 Ft^3 14.7
Start: Time 0621 Ft^3 11.6
Total: (min) 180 Ft^3 3.1

DuPont (DP)
Sampling rate (init.) ____ (ℓpm)
Sampling rate (final) ____ (ℓpm)
End: Time ________
Start: Time ________
Total: (min) ________

MSA (MSA)
Sampling rate (init.) ____ (ℓpm)
Sampling rate (final) ____ (ℓpm)
End: Time ____ Count ______
Start: Time ____ Count ______
Total: (min) ____ Count ______
ml/count ____________

Remarks ____________________

Volume Air/Cartridge 9 ℓ/cartridge

MAP:

Time ___ Temp. Wet. ___ Dry ________
Rel. Humid ___% Wind Dir./Speed __/__
Cloud ________ Odor ________
Remarks ____________

Time ___ Temp. Wet. ___ Dry ________
Rel. Humid ___% Wind Dir./Speed __/__
Cloud ________ Odor ________
Remarks ____________

Time ___ Temp. Wet. ___ Dry ________
Rel. Humid ___% Wind Dir./Speed __/__
Cloud ________ Odor ________
Remarks ____________

Time ___ Temp. Wet ___ Dry ________
Rel. Humid ___% Wind Dir./Speed __/__
Cloud ________ Odor ________
Remarks ____________

Figure D11. Field Sampling Protocol Sheet - A

TABLE D7. CHAIN OF CUSTODY RECORD

Research Triangle Institute
Analytical Sciences Division
Chemistry and Life Sciences Group
Research Triangle Park, NC 27709

SAMPLE CODE: 1637-ER-1-NULNCHSIPAK1	**Sample Type:** Airstream - Raw Wastewater	**Volume Collected:** 9 l/cart.
	No. of Containers: 3	**Volume Analyzed:** 9 l

Relinguished By:	Received By:	Time	Date	Operation Performed (aliquot, std. conc., remarks, etc.)
J. Jane	E. Pellizzari	9:30 AM	7/14/78	Preparation of Sampling Cartridges
E. Pellizzari	N. Doe	11:15 AM	7/24/78	Sampling of Airstream - Wastewater
N. Doe	D. Smith	10:00 AM	7/24/78	Addition of PFB/PFT as I (215/310 ng) to Sampling Cartridges
D. Smith	E. Pellizzari	4:30 PM	7/29/78	Analysis of Samples by GC/MS/COMP Data Output
E. Pellizzari	H. D. Wall	4:00 PM	8/15/78	Data Interpretation, Report to EPA

$$(2) \quad \mathrm{RMR}_{unk/std} = \frac{A_{unk}/g_{unk}/\mathrm{GMW}_{unk}}{A_{std}/g_{std}/\mathrm{GMW}_{std}}$$

A = peak area, as above
g = number of grams present
GMW = gram molecular weight

Thus, in the sample analyzed:

$$(3) \quad g_{unk} = \frac{A_{unk} \cdot \mathrm{GMW}_{unk} \cdot g_{std}}{A_{std} \cdot \mathrm{GMW}_{std} \cdot \mathrm{RMR}_{unk/std}}$$

Examples are given in Table D8.

192 The standards may be added as internal standards prior to sampling; however, since the volume of air taken for each sample is accurately known, it is also possible and more practical to use the external standard technique whereby the standard is introduced into the cartridge after sampling but prior to analysis. Previously, it has been determined that the retention times for these two compounds are such that they elute at approximately midpoint in the chromatographic run, and their retention time, as well as mass spectra, do not interfere with the analysis of the priority pollutants.

193 Since the volume of purge air taken to produce a given sample is accurately known, and an external stadnard is added to the sample, then the weight can be determined per cartridge, and hence, the concentration of the unknown per unit volume. The approach for quantifying the priority pollutants requires that the RMR is determined for each constituent of interest. This means that when a sample has been taken, the external standard must be added at a known concentration.

194 Results of analysis are expressed as ng/min/ft^2 pond surface for samples taken from open aeration systems and as ng/m^{3}for samples from closed chambers since the recovery of priority pollutants from raw wastewater or activated sludge is highly variable (1).

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1. E. D. Pellizzari. "Development of Method for Collection and Analysis of Consent Decree Purgeable Organics Emitted From Municipal Treatment Plants", EPA Contract No. 68-03-2681, October, 1978, 162 pp.

2. E. D. Pellizzari. "Development of Method for Carcinogenic Vapor Analysis in Ambient Atmospheres", EPA-650/2-74-121, July, 1974, 148 pp.

TABLE D8. EXAMPLES OF PREVIOUSLY DETERMINED RELATIVE MOLAR RESPONSE FACTORS FOR SEVERAL PRIORITY POLLUTANTS USING SELECTIVE M/Z IONS

Priority pollutant	*m*/*z*	iS-PFB (*m*/*z*-186)	iS-PFT (*m*/*z*-236)
methyl bromide	94	0.104 ± 0.008[a]	0.076 ± 0.002
dichloromethane	84	0.134 ± 0.002	0.104 ± 0.007
1,1-dichloroethylene	96	0.341 ± 0.049	0.249 ± 0.041
acrylonitrile	53	0.037 ± 0.005	0.027 ± 0.003
1,2-*trans*-dichloroethylene	61	0.098 ± 0.016	0.070 ± 0.007
chloroform	83	0.093 ± 0.013	0.071 ± 0.016
1,2-dichloroethane	98	0.016 ± 0.005	0.011 ± 0.001
1,1,1-trichloroethane	97	0.119 ± 0.004	0.095 ± 0.013
carbon tetrachloride	117	0.075 ± 0.005	0.054 ± 0.004
bromodichloromethane	127	0.017 ± 0.004	0.013 ± 0.003
1,2-dichloropropane	112	0.004 ± 0	0.032 ± 0.004
benzene	78	0.024 ± 0.032	0.187 ± 0.038
trichloroethylene	130	0.071 ± 0.017	0.052 ± 0.013
bromoform	171	0.036 ± 0.007	0.026 ± 0.004
tetrachloroethylene	170	0.019 ± 0.003	0.013 ± 0.002
toluene	93	0.019 ± 0.002	0.014 ± 0.002
ethylbenzene	106	0.254 ± 0.047	0.184 ± 0.036
chlorobenzene	112	0.341 ± 0.048	0.248 ± 0.039
1,2-dichlorobenzene	150	0.039 ± 0.002	0.0295 ± 0
1,3-dichlorobenzene	150	0.015 ± 0.001	0.0115 ± 0

[a] Average of triplicate determinations.

3. E. D. Pellizzari. "Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors", EPA-600/2-75-076, November, 1975, 186 pp.

4. E. D. Pellizzari. "The Measurement of Carcinogenic Vapors in Ambient Atmospheres", EPA-600/7-77-055, June, 1977, 288 pp.

5. E. D. Pellizzari. "Measurement of Carcinogenic Vapors in Ambient Atmospheres", EPA-600/7-78-062, April, 1978, 237 pp.

6. E. D. Pellizzari. "Improvement of Methodologies for the Collection and Analysis of Carcinogenic Vapors", EPA Contract No. 68-02-7264, in preparation.

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8. E. D. Pellizzari. "Analysis of Organic Air Pollutants by Gas Chromatography and Mass Spectroscopy", EPA-600/2-77-100, June, 1977, 104 pp.